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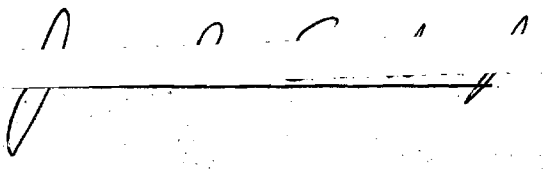

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COMPOSITION OF GROUP II ORGANOMETALLIC AND METAL HYDRIDE COMPOUNDS IN ETHER SOLVENTS

A THESIS

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The Faculty of the Graduate Division

by

James R. Robinson Sanders, Jr.

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THE COMPOSITION OF BERYLLIUM ALKYL-BERYLLIUM HALIDE AND BERYLLIUM ARYL-BERYLLIUM HALIDE MIXTURES IN DIETHYL ETHER

The composition of mixtures of dimethyl, diethyl and diphenyl beryllium compounds with beryllium chloride and beryllium bromide were studied in diethyl ether solvent. Selective precipitation, ebullioscopic molecular weight measurements, and nuclear magnetic resonance techniques were employed in this study. It was concluded that rapid redistribution does occur in mixtures of dialkyl or diaryl beryllium compounds with beryllium halides in diethyl ether solvent. Also, it was concluded that the equilibrium $R_2Be + BeX_2 \rightleftarrows 2\ RBeX$ lies predominantly to the right, and that the RBeX species were monomeric at low concentrations.

PART II

AN INVESTIGATION OF THE COMPOSITION OF ORGANOCADMIUM COMPOUNDS IN ETHER SOLVENTS

The interaction between $(n\text{-}C_4H_9)_2Cd$ and CdI_2 or $CdCl_2$ in diethyl ether and hydrocarbon solvents was investigated. Also, the products of the reaction between Grignard reagents and cadmium halides in 1:1 and 2:1 ratios were examined. In cyclohexane and diethyl ether, $(n\text{-}C_4H_9)_2Cd$ was found to interact more completely with CdI_2 than with

$CdCl_2$. A compound having the empirical formula n-C_4H_9CdX (X=Cl,I) was isolated. Molecular weight data for this species in solution could not be obtained. In 1:1 ratio, Grignard reagents (n-C_4H_9MgCl, n-C_4H_9MgI) were found to react with cadmium halides to yield magnesium halide and a mixture of the corresponding cadmium dialkyl and cadmium halide which interacted further as described above. Magnesium halides were observed to compete with cadmium halides in this latter interaction and the infrared spectra indicated a similar type of interaction for both halides. A compound having the elemental ratios Mg:Cd:X = 1:1:3 was isolated. In 2:1 ratio, Grignard reagents (n-C_4H_9MgCl, n-C_4H_9MgI) were found to react with cadmium halides ($CdCl_2$,CdI_2) in diethyl ether to produce magnesium halides and the corresponding dialkyl cadmium compound. Evidence was found for R_2Cd-MgX_2 interaction in the product mixtures when they were examined by infrared spectroscopy.

PART III

A STUDY OF THE REACTIONS OF LITHIUM ALUMINUM HYDRIDE AND SODIUM ALUMINUM HYDRIDE WITH BERYLLIUM CHLORIDE IN DIETHYL ETHER AND TETRAHYDROFURAN

The products of the reaction of $LiAlH_4$ and $NaAlH_4$ with $BeCl_2$ in diethyl ether and tetrahydrofuran solvents were studied by analysis, infrared spectroscopy and X-ray powder diffraction techniques. In diethyl ether solvent, two moles of $LiAlH_4$ react with one mole of $BeCl_2$ to produce BeH_2, LiCl and AlH_3. In 1:1 ratio in diethyl ether evidence was found for the products HBeCl and H_2AlCl. In tetrahydrofuran solvent, two moles of $NaAlH_4$ reacted with one mole of $BeCl_2$ to produce BeH_2, NaCl

and AlH_3. A similar result was obtained when using $LiAlH_4$ in tetrahydrofuran (2:1) except that all products were soluble in this case and a soluble complex $LiCl \cdot BeH_2$ was postulated. When $LiAlH_4$ and $NaAlH_4$ reacted with $BeCl_2$ in 1:1 ratio in tetrahydrofuran, the data indicated that the products were AlH_3, HBeCl and LiCl (or NaCl). No evidence for $Be(AlH_4)_2$ was found.

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THE COMPOSITION OF BERYLLIUM ALKYL-BERYLLIUM HALIDE AND BERYLLIUM ARYL-BERYLLIUM HALIDE MIXTURES IN DIETHYL ETHER

The composition of mixtures of dimethyl, diethyl and diphenyl beryllium compounds with beryllium chloride and beryllium bromide were studied in diethyl ether solvent. Selective precipitation, ebullioscopic molecular weight measurements, and nuclear magnetic resonance techniques were employed in this study. It was concluded that rapid redistribution does occur in mixtures of dialkyl or diaryl beryllium compounds with beryllium halides in diethyl ether solvent. Also, it was concluded that the equilibrium $R_2Be + BeX_2 \rightleftarrows 2\ RBeX$ lies predominantly to the right, and that the RBeX species were monomeric at low concentrations.

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The interaction between $(n\text{-}C_4H_9)_2Cd$ and CdI_2 or $CdCl_2$ in diethyl ether and hydrocarbon solvents was investigated. Also, the products of the reaction between Grignard reagents and cadmium halides in 1:1 and 2:1 ratios were examined. In cyclohexane and diethyl ether, $(n\text{-}C_4H_9)_2Cd$ was found to interact more completely with CdI_2 than with

PART I

THE COMPOSITION OF BERYLLIUM ALKYL-BERYLLIUM HALIDE AND BERYLLIUM ARYL-BERYLLIUM HALIDE MIXTURES IN DIETHYL ETHER

CHAPTER I

INTRODUCTION

Redistribution of dialkyl and diaryl organometallic compounds of Groups IIA and IIB with their corresponding halides has been the subject of much investigation for several years. In general, these systems are characterized by equilibrium 1 in ether solvents, where

$$R_2M + MX_2 \rightleftarrows 2\ RMX \qquad (1)$$

R = alkyl or aryl and X = halogen. Of necessity, associated forms of the species indicated must be included in any discussion; however, for simplicity they are not indicated here. The problem basically is whether this equilibrium lies to the right, the left, or whether an equilibrium involving alkyl exchange exists at all. Only recently have unambiguous and definitive results been reported for magnesium (3,4,5, 6,7,8) and zinc (9,10) in tetrahydrofuran and diethyl ether. The mercury alkyls and aryls have been known to redistribute with the corresponding halides, the reactions being an important method for preparation of organomercury halides. Definitive data concerning alkyl exchange in dialkyl cadmium-cadmium halide mixtures is lacking, although prior art exists indicating both nonexchange (11) and exchange (12). Part II of this thesis is concerned with the problem of alkyl exchange in R_2Cd-CdX_2 mixtures.

For the beryllium system, previous work (13), utilizing radioactive ^{7}Be in an exchange study between $(C_6H_5)_2Be$ and $^{7}BeBr_2$ showed that no exchange of the label occurs, $^{7}BeBr_2$ being recovered without loss of activity after precipitation from solution using 1,4-dioxane. On the other hand, the reaction between dimethyl beryllium and hydrogen chloride at 120-130° was reported (14) to yield methane and presumably methyl beryllium chloride, although this product was not well characterized. Head, *et al.* (15), reported the isolation of a volatile white solid from the reaction of $(t\text{-}C_4H_9)_2Be\cdot O(C_2H_5)_2$ and $BeCl_2$ which had the empirical formula $t\text{-}C_4H_9BeCl\cdot O(C_2H_5)_2$. However, this empirical formula is not inconsistent with the report above of no exchange since the compound could be dimeric, $(t\text{-}C_4H_9)_2Be\cdot BeCl_2\cdot 2(C_2H_5)_2O$. Bell and Coates (16), in the preparation of CH_3BeH from $(CH_3)_2Be$, $BeBr_2$, and LiH may have generated CH_3BeBr as an intermediate, since BeH_2 is insoluble in diethyl ether. However, reaction intermediates other than CH_3BeBr could explain the results and a dimeric or polymeric product $(CH_3)_2Be\cdot BeH_{2n}$ is consistent with no-exchange results.

Attempts to prepare alkyl beryllium halides directly from an alkyl halide and beryllium metal have met with questionable success. Gilman and Schulze (17) have reported the preparation of alkyl beryllium halides by reaction of beryllium with alkyl or aryl halides, at elevated temperatures for extended periods of time, using catalysts, such as mercuric chloride, beryllium chloride, iodine, and bromine. Identification of the products was by color test with Michler's ketone; no analytical data were presented. Russian workers (18) also have reported the reaction of alkyl halides with beryllium, above room

temperature. These reported syntheses suffer from a lack of definitive data concerning the composition of the products and must be considered inconclusive with respect to the definition of an alkyl beryllium halide species.

In view of the fact that the alkyls and aryls of magnesium, zinc, mercury and possibly cadmium, exhibit redistribution with their halides in ether solvents, a reinvestigation of the beryllium case seemed to be warranted, since this system would be expected to behave similarly.

CHAPTER II

EXPERIMENTAL AND INSTRUMENTATION

Note: Beryllium and its compounds are extremely toxic. Any work with these materials should be conducted according to the established safe-handling procedures (19).

Reagents

Beryllium was obtained from the Brush Beryllium Co., Elmore, Ohio, as high purity electrorefined flake. Impurities, in parts per million, are listed as follows: BeO (0.3%); C, 140; B, -1; Al, 13; Cr, 80; Fe, 30; Mg, 20; Mn, 6; Ni, -8; Na, 110; Ca, -85; Cu, 30; Si, 40; Zn, -55; Cl, 1900; Be, balance. Before use, the metal as obtained was dried in a current of warm, dry nitrogen.

Dimethylmercury, diethylmercury, and diphenylmercury were obtained from Metallomer Labs. The entire sample of diethylmercury obtained from the above source was distilled at 157-158° (756 mm) and found to contain no contaminating impurity. Dimethylmercury and diphenylmercury were used without further purification.

Bromine was Matheson, Coleman and Bell ACS reagent grade, used without further purification. Chlorine was Matheson high purity and was also used without further purification.

Butyllithium as a 1.6 M solution in hexane was obtained from Foote Mineral Co. The reagent was standardized for C-bound Li and transferred volumetrically.

Phenyl iodide was Eastman reagent, distilled before use at reduced pressure. Solvents were all reagent grade: $(C_2H_5)_2O$ was distilled from $LiAlH_4$ and 1,4-dioxane from $NaAlH_4$ immediately prior to use. Benzene was also distilled from $NaAlH_4$ at atmospheric pressure.

Analytical

Halide analyses were performed by the Volhard method. Beryllium was determined using an empirical titrimetric procedure (23). According to this procedure, beryllium hydroxide is precipitated from aqueous solution at pH 8.5, using NaOH. Excess NaF is added to form the weakly ionized BeF_2, liberating hydroxyl ions which are titrated with H_2SO_4 to the phenolphthalein end point. The measured released alkalinity is proportional to the amount of Be present.

Preparative Methods

General

All operations were conducted in an atmosphere of dry, oxygen-free nitrogen. Transfers of reagents were made in a nitrogen-filled drybox equipped with a special recirculating system to remove oxygen (manganese oxide) and moisture (dry ice-acetone traps). Details of the oxygen removal system are given by Shriver (20). Glassware was heated, and then dried under a stream of dry nitrogen immediately before use.

Beryllium Halides

Preparation of beryllium halides by direct combination of halide and metal in diethyl ether was found to yield significant quantities of halogenated solvent as a by-product. Beryllium bromide in diethyl

ether prepared in this manner becomes badly discolored on standing (dark brown) and gas chromatographic analysis of the hydrolysate confirms the presence of numerous impurities (brominated ethers). Also, nmr spectra of solutions of this crude halide exhibit complexity of the ether bands attributable to the presence of halogenated solvent. Recrystallization and disposal of the supernatant liquor was not completely effective in removing the impurities after three recrystallizations of the $BeBr_2$.

Beryllium chloride and bromide in very pure form were prepared by direct reaction of the elements.* The reaction was carried out in a reactor and collecting vessel which consisted of a Pyrex glass reacting tube connected to a 250-ml, round-bottomed flask via a narrow neck, which was sealed with a torch at the completion of the synthesis. Chlorine or bromine in a slow nitrogen stream was passed over 0.25 g of beryllium flake (28 mmoles) in the reactor tube. The tube and beryllium were heated with a grid burner and the product, formed as a white, microcrystalline smoke, was swept through the restriction into the collecting flask where it collected as a fluffy deposit. A second burner served to keep the product moving swiftly and prevented plugging at the restriction. The receiving flask was vented adequately and a plug of glass wool in the neck of the flask prevented loss of the finely divided product. After the reaction had subsided and little product continued to be formed, the halogen supply was cut off and the apparatus was

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*We are indebted to Professor G. E. Coates, University of Durham, Durham, England, for calling this method of preparation of $BeCl_2$ to our attention. This method was also used for the preparation of $BeBr_2$. See also, G. B. Wood and A. Brenner, *J. Electrochem. Soc.*, *104*, 24 (1957).

allowed to cool under the slow flush of dry nitrogen. All connections were standard taper glass joints. The use of larger quantities of beryllium metal resulted in correspondingly larger quantities of voluminous product and a larger receiving flask was used.

It was found in later syntheses that the substitution of argon for nitrogen in this reaction is preferred. With argon the reaction is essentially quantitative and the residue of black solid, observed in the experiments where nitrogen was used, is avoided.

Ethereal solutions of the halides were prepared by adding the anhydrous halide, in small quantities, to cold diethyl ether. Vigorous reaction was noted, presumably due to release of the heat of solvation. The resulting solutions were clear and colorless and a two-phase mixture was formed when the solubility limit was exceeded. Gas chromatography and nmr spectra indicated that impurities were, and the solutions appeared to be, stable when tightly sealed and stored wrapped in aluminum foil. The Be:Cl ratio of $BeCl_2$ in ether solution was found by elemental analysis to be 1.0:2.04 and the Be:Br ratio of an ether solution of $BeBr_2$ was found to be 1.0:1.96.

Beryllium-7 Metal

^{7}Be metal was obtained by bombardment in the Berkeley 88-in. cyclotron of a 1 g sample of Be metal by 30 MEV deuterons for approximately 100 μA hr. We are indebted to Drs. B. G. Harvey and Ruth Larimer of the Lawrence Radiation Laboratory, University of California, Berkeley, California, for the samples.

Dimethylberyllium

After a modification of the method of Burg and Schlesinger (21), 2.5 g of beryllium flake were placed in a 100-ml round-bottomed flask fitted with a small water-cooled condenser and vented to a dry nitrogen line. A small teflon-coated stirring bar and 15 ml of $(CH_3)_2Hg$ were added and the mixture was refluxed, with stirring, at 110°C in an oil bath. After 168 hr., the beryllium was heavily amalgamated, white crystals of $(CH_3)_2Be$ were evident, and the reaction had apparently stopped. In a subsequent synthesis, it was found that the addition of a crystal of $(CH_3)_2Be$ and a small drop of Hg to the reaction mixture shortened the reaction time to 90 hr. Residual dimethyl mercury was removed at reduced pressure at 100°C and the product was vacuum sublimed at 130°C for 12-20 hr. The sublimate is a gray crystalline mass, the color being due to included elemental Hg. This material was dissolved in diethyl ether with little noticeable heat of solvation to give a clear, colorless solution, stable in tightly sealed flasks in the dry-box. The nmr spectrum of this solution at 35°C exhibits a sharp singlet at 70 cps upfield from internal TMS, in addition to well-defined solvent bands. No change in the nmr spectrum was noticeable on prlonged storage or in a sample exposed briefly to the air to ascertain the effects of slight oxidation. Solutions of $(CH_3)_2Be$ are extremely reactive and fume vigorously in air. A qualitative test for residual soluble Hg in the reagent was negative using ferrocyanide and 2,2'-dipyridyl. Standard solutions of $(CH_3)_2Be$ in diethyl ether were prepared by slowly adding the beryllium compound to a solution of cold diethyl ether and analyzing the solution for beryllium. The analysis was made for moles of beryllium

per gram of solution, to yield molal concentration.

Diphenylberyllium

Attempted preparation of diphenylberyllium from beryllium flake and diphenylmercury, in a manner similar to the preparation of dimethylberyllium, proved unsatisfactory in the absence of a catalyst at 150°C. The addition of a pea-sized piece of $HgCl_2$ after 48 hr. was followed by the amalgamation of the Be metal to some extent; however, after 288 hr. reaction time followed by extraction of the product with o-xylene (13), very little product was isolated.

Diphenyl beryllium was successfully synthesized by the reaction of C_6H_5Li with $BeCl_2$ in diethyl ether (27). Ethereal C_6H_5Li was synthesized in a very pure form using a modification of the procedure of Schlosser and Ladenburger (22). In a 2-l flask, 178.6 mmoles of C_6H_5Li in diethyl ether were added to 89.3 mmoles of $BeCl_2$ in diethyl ether, giving a reaction volume of 1236 ml. A white precipitate of LiCl formed immediately. The mixture was stirred for 40 hr. at 25°C. LiCl was removed by filtration through a coarse frit, and a clear, colorless solution was obtained. The completion of reaction was indicated by Cl^- analysis of the resulting solution. Analysis for residual Cl^- indicated a concentration of 2.4×10^{-3} M. The nmr spectrum of the product is clearly different from that of C_6H_5Li, in that the observed absorptions lie closer to the benzene resonance and the o-H resonance is broadened into a wide band.

Diethylberyllium

In a typical synthesis, 0.2 mole of $(C_2H_5)_2Hg$ and 0.2 mole of Be were combined in a flask fitted with a condenser. Approximately

0.05-0.1 g of $HgCl_2$ was added as a catalyst, and the mixture heated at 125°C for 36 hr. At the end of this time, a mercury pool had formed and the reaction appeared to be complete. The product was purified by vacuum distillation at 60°C (150 μ) (lit. 63°C at 300 μ). The distilled $(C_2H_5)_2Be$ was stored as the neat liquid. A qualitative test for residual mercury using ferrocyanide and 2,2'-dipyridyl was negative. A 4-ml sample of $(C_2H_5)_2{}^7Be$ prepared by this method produced 8.5×10^5 dps.

Dehydration of $BeCl_2$

Be metal was dissolved in dilute aqueous HCl and then the liquid was evaporated to yield the solid white hydrate of $BeCl_2$. The hydrate was refluxed with freshly distilled $SOCl_2$ for 20 min. and then excess $SOCl_2$ was removed at reduced pressure. Analysis of the solid product gave the elemental ratio: Be:Cl = 1.07:1.0.

Precipitation Studies

1,4-dioxane, freshly distilled from $NaAlH_4$, was added to ethereal solutions of $(CH_3)_2Be$, $BeBr_2$, and equimolar mixtures of $(CH_3)_2Be$, $(C_2H_5)_2Be$, and $(C_6H_5)_2Be$ with $BeCl_2$ and $BeBr_2$. $BeBr_2$ yielded an insoluble dioxanate instantly. $(CH_3)_2Be$ gave a slowly forming precipitate which was soluble in excess diethyl ether. In the case of the mixtures, a measured quantity (by syringe) of 1,4-dioxane was added per millimole of beryllium present in the solution, and the mixture was stirred for at least 3 hr. All mixtures produced slowly forming white precipitates. For the methyl and phenyl systems, the precipitate was isolated by filtration through a medium frit glass sintered funnel. The filtrates were analyzed for beryllium and halogen after hydrolysis of the samples. Analytical data are summarized in Table 1.

Physical Measurements

Molecular Association Measurements

The apparent molecular weights of the beryllium compounds and mixtures of beryllium compounds prepared in this study were determined ebullioscopically in diethyl ether at 760 mm pressure, using a modified Cottrell boiling point elevation apparatus. Temperature changes were observed using a Beckmann differential thermometer and the pressure was measured using a precision Wallace-Tiernan manometer. Solvent loss was prevented by using recirculated ice-water in the condenser of the apparatus. Solvent and standardized sample solutions were introduced by weight, through a septum cap, using tared syringes. Details of the operation of this apparatus have been previously described in detail by Walker (24,25). Association results are expressed as i values (apparent molecular weight/formula weight).

Nmr Studies

Spectra were recorded on a Varian Associates A60 (60mc) spectrometer with variable temperature probe. The probe was calibrated using the temperature-dependent resonance in CH_3OH.

Volumetrically prepared samples from standardized solutions were introduced into carefully dried nmr tubes in the drybox, and capped tightly. Comparison spectra using internal and external tetramethylsilane (TMS) were identical; the internal standard was preferred because of greater reliability of temperature equilibrium being attained by both sample and reference, and obvious operational simplicity. No evidence of solute-TMS reactivity was observed.

CHAPTER III

RESULTS AND DISCUSSION

Earlier studies concerned with redistribution in the system $R_2Be + BeX_2$ were centered around isotopic labeling experiments (13). The exact system studied involved solution of diphenylberyllium with $^7BeBr_2$ in diethyl ether followed by precipitation of $BeBr_2$ from solution as the dioxanate. It was then determined that no exchange had taken place in solution since the ^7Be label was not statistically distributed between the $(C_6H_5)_2Be$ and $BeBr_2$ after precipitation of the $BeBr_2$. Equation (2) represents the expected course of the reaction for both exchange and no-exchange results.

$$(C_6H_5)_2Be + {}^7BeBr_2 \underset{\longleftarrow}{\overset{\text{exchange}}{\longrightarrow}} C_6H_5BeBr + C_6H_5{}^7BeBr$$

$$\begin{array}{lll} \text{no exchange} \downarrow & \text{dioxane} & \downarrow \text{dioxane (2)} \\ (C_6H_5)_2Be + {}^7BeBr_2\cdot\text{dioxane} & & (C_6H_5)_2{}^7Be + {}^7BeBr_2\cdot\text{dioxane} \\ \text{in solution} \quad \text{ppt} & & (C_6H_5)_2Be \quad BeBr_2\cdot\text{dioxane} \\ & & \text{in solution} \quad \text{ppt} \end{array}$$

An attempt to repeat the prior isotopic labeling work led to a very unusual result. First of all, the system studied was $(C_2H_5)_2{}^7Be + BeBr_2$ rather than $(C_6H_5)_2Be + {}^7BeBr_2$. The reasons for this are the following:

a. $(C_2H_5)_2Be$ is a liquid which can be obtained very pure by vacuum distillation, whereas $(C_6H_5)_2Be$ is a solid which, by the method of preparation reported, could not be obtained pure.

b. Putting the isotope label in the R_2Be rather than the BeX_2 has several obvious advantages from a purity and convenience standpoint. It is of course very important that in such isotopic labeling studies that all starting materials be exceptionally pure since a trace impurity might catalyze or prevent redistribution and give misleading results. In this respect much care was given to the preparation of the starting materials used in this study. The $(C_2H_5)_2{}^7Be$ was prepared from distilled $(C_2H_5)_2Hg$ and electro-refined beryllium (99.7% purity) in admixture with ^7Be and the resulting product distilled prior to use. The $BeBr_2$ was prepared as a white crystalline solid from beryllium metal and bromine in a hot tube reaction and purified by sublimation prior to use.

On admixture of standard diethyl ether solutions of $(C_2H_5)_2{}^7Be$ and $BeBr_2$ followed by dioxane precipitation, it was surprising to find that no $BeBr_2$ but a product of empirical formula C_2H_5BeBr precipitated. Fractional precipitation of the product by adding incremental amounts of dioxane produced fractions of a white solid that in each case had a Be:Br ratio of 1:1. Such a result precludes the validity of an isotopic labeling experiment such that earlier reports could not be considered valid provided the $(C_6H_5)_2Be$-$BeBr_2$ system behaves in the same manner. The data to be presented later show that this is the case.

Another factor that appears to invalidate the earlier isotopic labeling study is concerned with the preparation of the $^{7}BeBr_2$. In the earlier study ^{7}Be was dissolved in aqueous HCl to form $^{7}BeCl_2 \cdot nH_2O$. The halide was then reported to undergo dehydration by refluxing with $SOCl_2$. The resulting product was then diluted with $BeBr_2$ (prepared from Be and Br_2 in diethyl ether) to form the reported $^{7}BeBr_2$. We have found that adding aqueous HCl to Be metal to form $BeCl_2 \cdot nH_2O$ proceeds readily; however, refluxing this with $SOCl_2$ does not produce anhydrous $BeCl_2$, but what appears to be beryllium oxychloride (Be:Cl ratio of the product was found to be 1:1). The oxychloride is insoluble in diethyl ether and thus if the label actually was in the form of insoluble beryllium (7) oxychloride, solution with $(C_6H_5)_2Be$ might not have had a chance to be effected and addition of dioxane simply resulted in the filtration of the insoluble beryllium (7) oxychloride (with precipitated $(C_6H_5BeBr)_n$) with all of the radioactive material appearing in the precipitate.

A third complication of the earlier method used was the preparation of $BeBr_2$ used for the dilution of the labeled halide. In the earlier method, bromine was added to beryllium metal in diethyl ether to form ether-soluble $BeBr_2$. In studying this reaction we have found that diethyl ether is highly brominated (vpc analysis of hydrolyzed solution) during the course of this reaction although the resulting solution appears clear and colorless temporarily. Since a beryllium alkyl or aryl might be expected to react with an α-bromo ether, this factor also brings uncertainty into the earlier method used. Thus, from the reasons presented above, it appears clear that the conclusions

drawn earlier from the isotopic labeling experiment indicating no redistribution in the system $(C_6H_5)_2Be$-$BeBr_2$ are highly questionable.

Since a solution of $(C_2H_5)_2Be$ and $BeBr_2$ deposited solid fractions of empirical formula C_2H_5BeBr on fractional precipitation with dioxane, it is evident that redistribution in the system would be established if the product could be shown to be monomeric in solution. It is also clear that redistribution might be detected by low-temperature nmr studies provided separate signals can be detected for the R_2Be and RBeX compounds. In the ensuing discussions are presented the results of: (a) selective precipitation studies of solutions of R_2Be and BeX_2 compounds using 1,4-dioxane; (b) molecular association studies of R_2Be, BeX_2 and R_2Be-BeX_2 mixtures; (c) low-temperature nmr studies of R_2Be and R_2Be-BeX_2 mixtures. These studies were carried out using $(CH_3)_2Be$, $(C_2H_5)_2Be$, and $(C_6H_5)_2Be$ as the alkyl or aryl beryllium compound and $BeCl_2$ and/or $BeBr_2$ as the beryllium halide in diethyl ether solvent.

Precipitation Studies

Table 1 summarizes the results of 1,4-dioxane addition to equimolar (1:1) mixtures of $(CH_3)_2Be$ and $(C_6H_5)_2Be$ with $BeCl_2$ and $BeBr_2$ in diethyl ether. It is clear from the data that a species of empirical formula RBeX is being precipitated as the dioxanate. From the experimental stoichiometry of the precipitation reaction, a monodioxanate is formed, and residual beryllium is found in the supernatant liquid.

These results show clearly that BeX_2 is not being precipitated

Table 1. Precipitation Studies. Addition of Dioxane to R_2Be-BeX_2 Mixtures in Diethyl Ether

R_2Be-BeX_2		Initial Be:X Ratio	Be Present, mmol	Dioxane Added, mmol	Be:X Ratio		Residual Be in Soln, %
R	X				Ppt	Filtrate	
CH_3	Cl	1.02:1	3.3	1.65	1:1.16	1.29:1	50
CH_3	Br	1:1.02	4.6	2.3	1:1.05	1:1.04	50
C_6H_5	Br	1.04:1	2.6	1.3	1.06:1	1.04:1	50

selectively, in a manner analogous to the behavior of MgX_2-R_2Mg mixtures toward dioxane. This discovery invalidates the use of dioxane precipitation to recover BeX_2 in the radioactive labeling experiments attempted by ourselves and others (13). Similar findings have been reported (10) for the systems $(C_2H_5)_2Zn$-ZnI_2 in tetrahydrofuran and diethyl ether, and $(C_2H_5)_2Zn$-$ZnBr_2$ in diethyl ether. Here, the precipitate found using tetramethylethylenediamine (TMED) gave the empirical formula RZnX·TMED. However, it was also found that $(C_2H_5)_2Zn$-$ZnBr_2$ in THF precipitated $ZnBr_2$·TMED.

When dioxane was added to a diethyl ether solution of $BeCl_2$ or $BeBr_2$, an immediate precipitate of the BeX_2 dioxanate was obtained. On the other hand, when dioxane was added to a solution of $(CH_3)_2Be$ or $(C_6H_5)_2Be$ precipitation of the R_2Be dioxanate was very slow and complete precipitation took place only after a large excess (three- to tenfold) of dioxane was added. In contrast, when dioxane was added to the R_2Be-BeX_2 mixtures precipitation was relatively slow. The results indicate that if the solution contained a mixture of R_2Be and BeX_2, the BeX_2 should have precipitated first and rapidly leaving in solution the relatively soluble R_2Be dioxanate, especially under the conditions used when the Be:dioxane ratio was 2:1.

The precipitation data are consistent with equilibrium 1, although nothing can be said about the position of the equilibrium. Unfortunately, the precipitation data alone do not distinguish between RBeX and $(RBeX)_2$. Since the dimer can be represented by the species R_2Be·BeX_2, it is necessary to know the molecular weight of the species in solution in order to resolve this ambiguity.

Molecular Weight Measurements

The ebullioscopically determined association data (i-values) of the compounds and mixtures studied in diethyl ether at 36° are shown in Table 2 and plotted in Figures 1, 2, and 3. It is seen that over the concentration range studied, the species are monomeric when calculated as R_2Be, BeX_2, and RBeX. Also, the degree of molecular association is seen to increase slightly with increasing concentration, as expected. The association determinations were made in the same concentration range as the dioxane precipitation studies. The low solubility of $BeBr_2$ prevented study over a wider concentration range.

The precipitation and molecular weight data indicate that equilibrium 1 lies predominantly to the right, as the redistributed species RBeX. It must be recognized that the average molecular weight produced by the experiment excludes only associated species from equilibrium 1 and that removal of a 1:1 precipitate from the mixture implies that RBeX is present as the predominant species. If significant quantities of BeX_2 were present, the halide dioxanate would be expected to precipitate preferentially because of the preferential reaction of BeX_2 with dioxane compared to the other less acidic species in solution and because of the greater insolubility of the BeX_2 dioxanate. Also, enhanced solubility of the beryllium halides in the presence of $(CH_3)_2Be$ and $(C_6H_5)_2Be$ demonstrates that appreciable interaction occurs; since the interaction is not association, it must be the result of redistribution.

The precipitation of $ZnBr_2$·TMED discussed above suggests that in this case, equilibrium 3 may favor either the mixture $R_2Zn + ZnX_2$,

Table 2. Molecular Weight Data for R_2Be, BeX_2, and R_2Be-BeX_2 Mixtures in Diethyl Ether

R_2Be-BeX_2 (Ratio)	Concn Range, m	i
$(CH_3)_2Be$	0.152-0.428	0.88-0.94
	0.104-0.381	0.92-0.97
$(CH_3)_2Be$-$BeBr_2$(1:1)	0.056-0.255	1.01-0.35
	0.81-0.201	1.01-1.22
$(CH_3)_2Be$-$BeCl_2$(1:1)	0.031-0.123	0.83-0.99
$(C_6H_5)_2Be$	0.039-0.138	0.90-0.98
$(C_6H_5)_2Be$-$BeBr_2$(1:1)	0.035-0.130	0.92-1.1
$BeCl_2$	0.040-0.115	0.91-1.1
$BeBr_2$	0.037	0.91

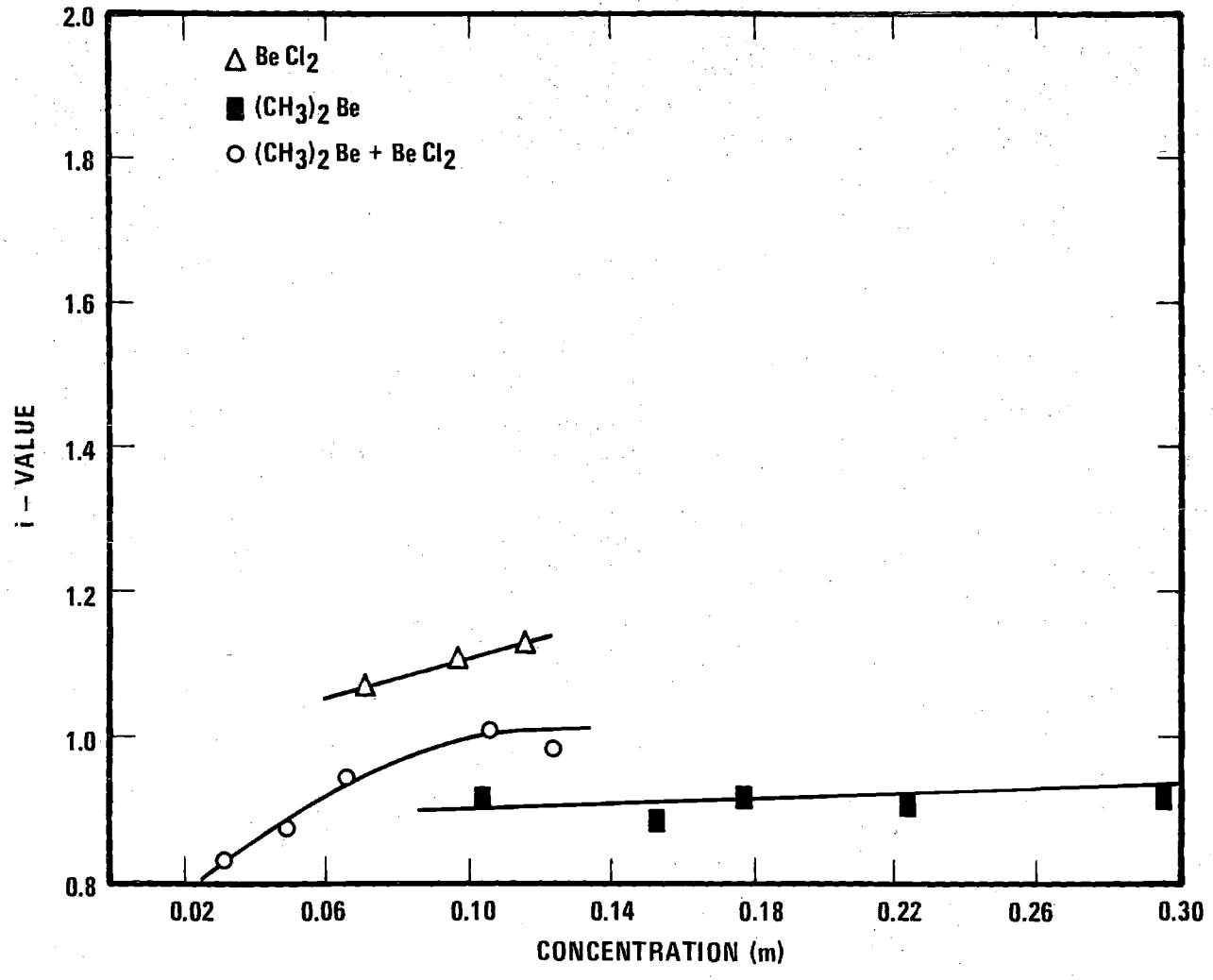


Figure 1. Association of $BeCl_2$, $(CH_3)_2Be$, and $(CH_3)_2Be + BeCl_2$ in Diethyl Ether

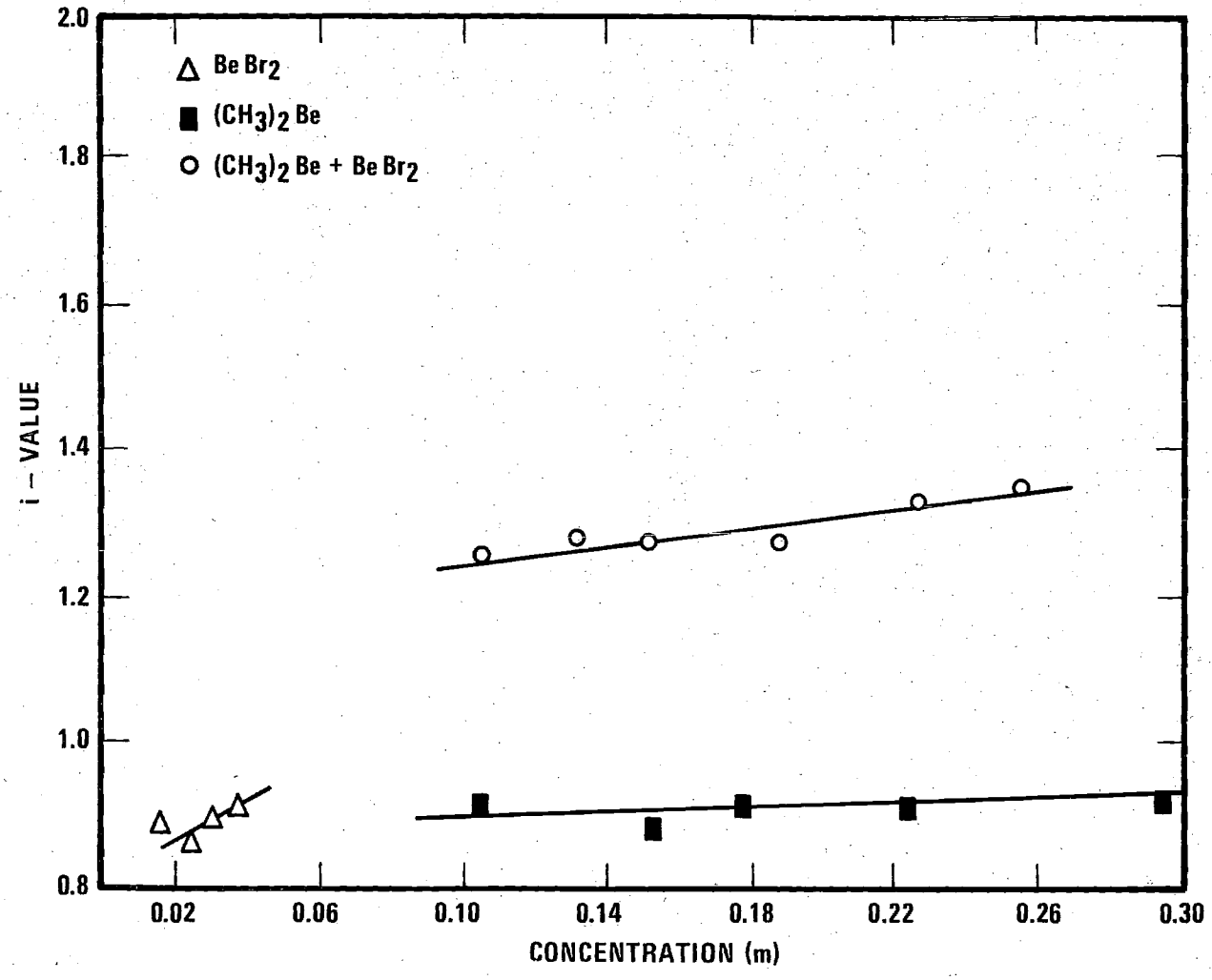


Figure 2. Association of $BeBr_2$, $(CH_3)_2Be$ and $(CH_3)_2Be + BeBr_2$ in Diethyl Ether

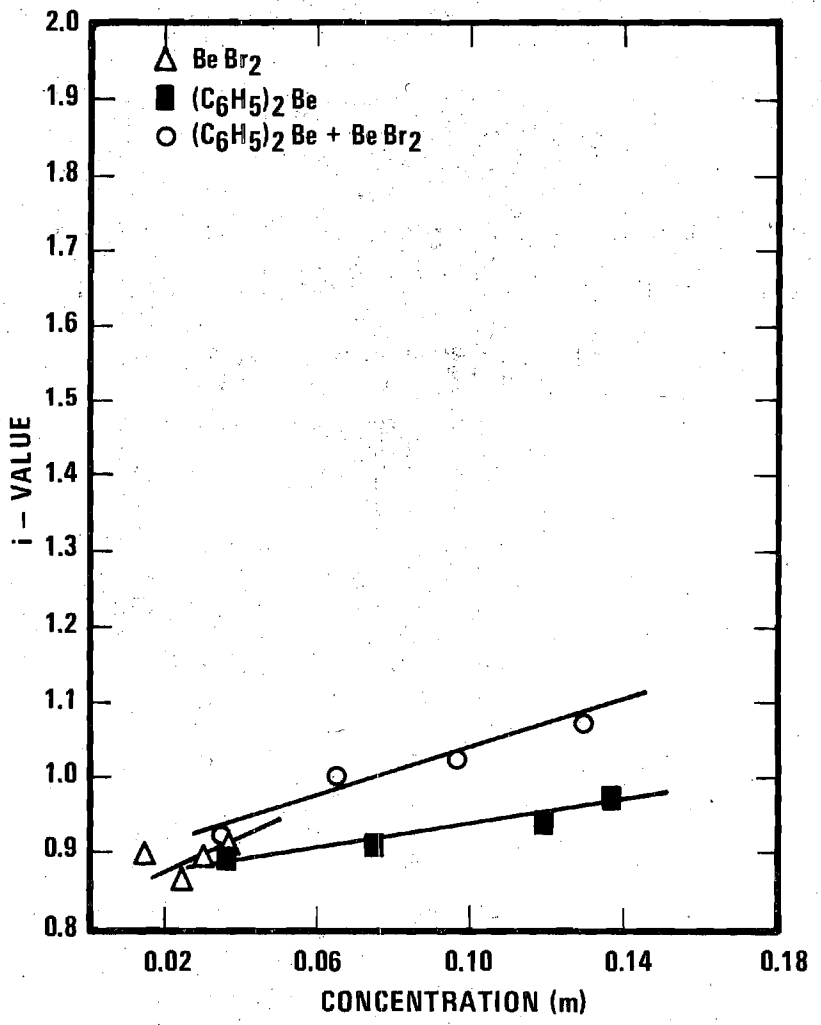


Figure 3. Association of $BeBr_2$, $(CH_6H_5)_2Be$, and $(C_6H_5)_2Be + BeBr_2$ in Diethyl Ether

$$(C_2H_5)_2Zn + ZnBr_2 \rightleftharpoons 2\ C_2H_5ZnBr \qquad (3)$$

or that the equilibrium may be facile enough, compared to complexation and precipitation, that the complexed halide is deposited preferentially. Similar arguments apply for organomagnesium systems. For these systems, the MgX_2·ligand adducts are the least soluble species which would be expected to precipitate on addition of a strong base (ligand) (26). When monomeric RMgX products were precipitated instead, the conclusion was that the equilibrium lay entirely in the direction of the RMgX species. Factors which would be expected to determine the position of equilibria in these systems are solvent basicity, nature of halogen, and alkyl or aryl substituent.

Nmr Investigations

Tables 3 and 4 summarize the data for low-temperature studies for $(CH_3)_2Be$-BeX_2 mixtures (X = Cl, Br) in diethyl ether. The values in the table are the chemical shifts of the CH_3-Be resonance singlet, upfield from TMS, in cycles per second (cps). The spectra for the system $(CH_3)_2Be$-$BeCl_2$ are reproduced in Figure 4.

The second column of Table 3 shows a low-temperature profile of $(CH_3)_2Be$ in diethyl ether. The position of the signal is markedly temperature dependent. The fact that only one signal is observed at -75°C is indicative of the fact that $(CH_3)_2Be$ is not associated, otherwise two signals of equal intensity would have been expected--one signal for the two terminal methyls and one signal for the two bridging

Table 3. Chemical Shift of CH_3-Be Singlet Upfield from TMS in Cycles per Second for Mixtures of $(CH_3)_2Be$ and $BeBr_2$ in Diethyl Ether

T, °C	Ratio $(CH_3)_2Be:BeBr_2$			
	1:0	1:1	2:1	1:2
35	70.5	71	71	71
0	71	71	71.5	71
-15	71.5	72	72	72
-30	72.5	74	72.5	73
-45	74	73.5	73.5	74
-60	76	74.5	74.5	75
-75	78	75	75,79	75

Table 4. Chemical Shift of CH_3-Be Singlet Upfield from TMS in Cycles per Second for Mixtures of $(CH_3)_2Be$ and $BeCl_2$ in Diethyl Ether

	Ratio $(CH_3)_2Be:BeCl_2$			
T, °C	1:0	1:1	2:1	3:1
35	70	75	72.5	72
0	70.5	76	74.5	73.5
-45	74.5	79	76	75.5
-85	86	82	81,86.5	81.5,86.5

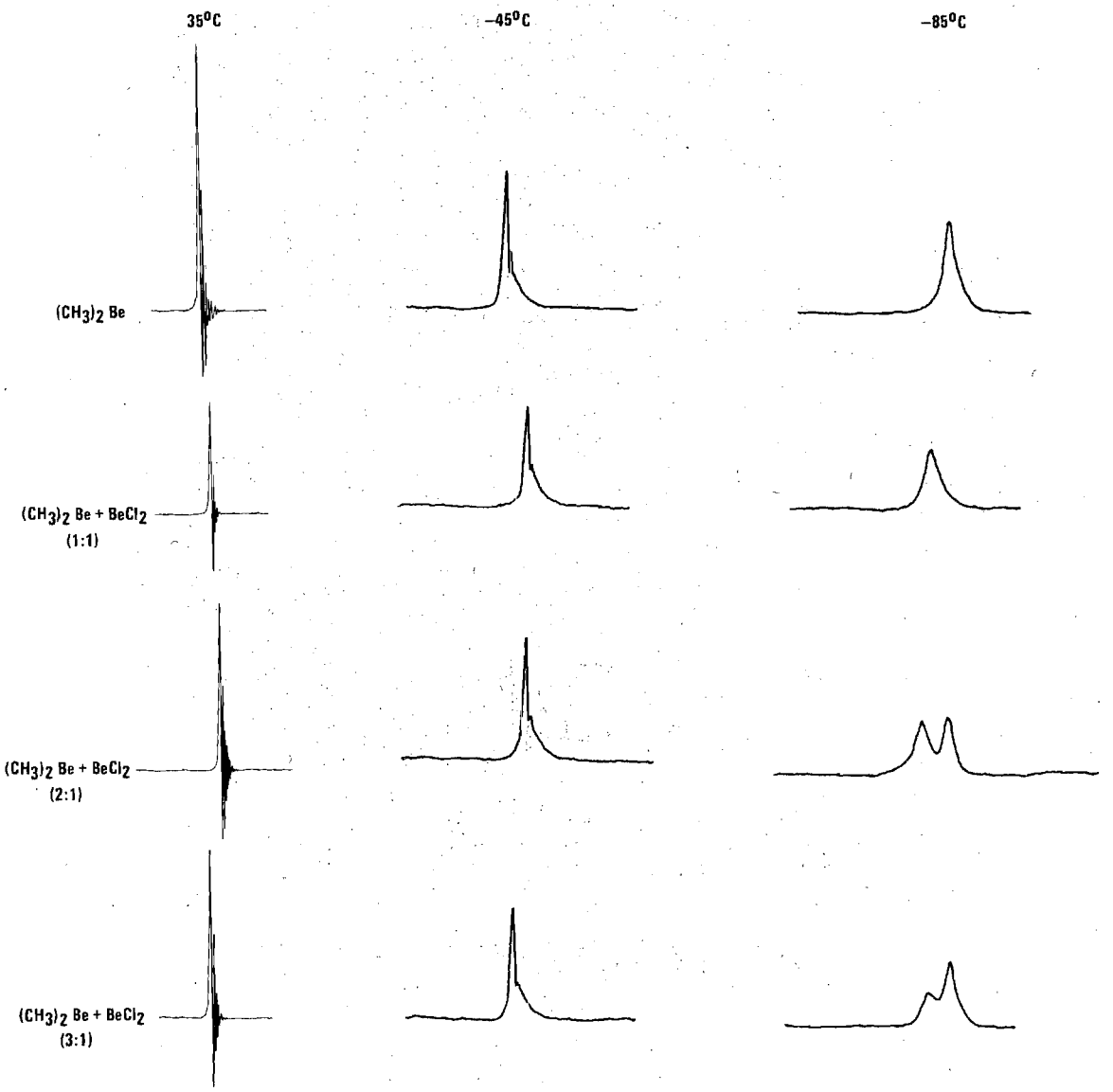
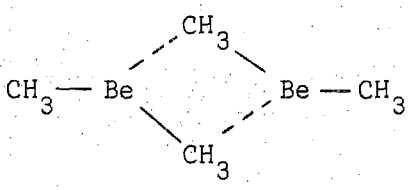


Figure 4. Nmr Spectra of $(CH_3)_2Be$ and Mixtures of $(CH_3)_2Be$ + $BeCl_2$ in 1:1, 2:1, and 3:1 Ratios in Diethyl Ether

methyl groups.* When $(CH_3)_2Be$ and $BeBr_2$ were allowed to



equilibrate in 1:1 ratio, only one signal was observed at -75°C; however, it was at a position 3 cps downfield from that of $(CH_3)_2Be$ at the same temperature. Such a small difference is not very meaningful; however, the fourth column showing the results of the 2:1 ratio shows two signals at -75°C. One signal is indicative of excess $(CH_3)_2Be$ and thus the other signal (present also at 1:1 ratio) is indicative of CH_3BeBr. The fact that $BeBr_2$ precipitated from the mixture at -75°C in 1:2 ratio, while no precipitate occurred in 1:1 ratio, indicates once again that there is little association among the species in solution.

The results of the $(CH_3)_2Be$-$BeCl_2$ nmr study are even more convincing (Table 4, Figure 4). At 35°C only an average signal is observed for all of the mixtures due to the rapid exchange at this temperature. When $(CH_3)_2Be$ and $BeCl_2$ are in 1:1 ratio only one signal is observed at -85°C which is displaced 4 cps downfield from the $(CH_3)_2Be$ signal at the same temperature. Once again the convincing experiments are

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*This assumes that alkyl exchange is slow on the nmr time scale at -75°C. Such observations representing association have been made for $(CH_3)_3Al$ in cyclopentane, whereas in diethyl ether only one resonance signal is observed since $(CH_3)_3Al$ is monomeric in this solvent.

the nmr observations at 2:1 and 3:1 ratios. When $(CH_3)_2Be$ and $BeCl_2$ are in 2:1 ratio, two signals are observed; one is characteristic of $(CH_3)_2Be$ and the other for what must be CH_3BeCl since the signals bear a 1:1 ratio. When $(CH_3)_2Be$ and $BeCl_2$ are combined in 3:1 ratio, the signal indicative of $(CH_3)_2Be$ increases and the signal indicative of CH_3BeCl remains unchanged. Thus the nmr evidence alone appears conclusive to establish redistribution in the $(CH_3)_2Be$-BeX_2 systems.

The nmr spectra of similar mixtures of $(C_6H_5)_2Be$-$BeBr_2$ were also determined. The spectra obtained are qualitatively like those found for C_6H_5Li, $(C_6H_5)_2Mg$ and $(C_6H_5)_2Zn$ (27). The effect of replacing a phenyl group by halogen was observed in slight upfield shifts of the bands, but the complexity of the AB_2C_2-type pattern made detailed and clear-cut analysis of the variable temperature beyond the scope of the present work.

CHAPTER IV

CONCLUSIONS

The conclusions therefore are that the nmr evidence, in addition to selective precipitation and association studies, indicates strongly that rapid redistribution in the system R_2Be-BeX_2 where R = CH_3, C_2H_5, C_6H_5 and X = Cl, Br does take place in diethyl ether solvent. It is also concluded from this study that equilibrium 1 lies predominantly to the right.

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PART II

AN INVESTIGATION OF THE COMPOSITION OF ORGANOCADMIUM COMPOUNDS IN ETHER SOLVENTS

CHAPTER I

INTRODUCTION

In the organometallic chemistry of the Group IIB metals, the understanding of the behavior of organomercury and organozinc systems is greatest. The organometallic chemistry of cadmium, on the other hand, is less well-defined. This may be due in part to the characteristic instability of many organocadmium compounds.

Two areas of current interest in organocadmium chemistry are: (a) the solution composition of RCdX compounds, represented by Equation 1, and (b) the solution composition of alkyl cadmium compounds in the presence of cadmium, magnesium, aluminum, and lithium halides.

$$R_2Cd \cdot CdX_2 \rightleftharpoons R_2Cd + CdX_2 \rightleftharpoons 2RCdX \qquad (1)$$

(where R = alkyl, aryl; X = Cl,Br,I)

Redistribution reactions in ether solvents and solution composition of $R_2M\text{-}MX_2$ mixtures have been actively investigated for Groups IIA and IIB during the last ten years. Definitive results have been published, establishing the reality of alkyl (or aryl) exchange for beryllium (2), magnesium (3), zinc (4), and mercury alkyls (5), with their corresponding metal halides according to Equation 1.

While published efforts supporting the redistribution of dialkyl (or aryl) cadmium with cadmium halides to form the species

RCdX in solution have appeared recently, we feel that the data do not justify the conclusions. The background is summarized below.

The first investigation concerning redistribution in the R_2Cd-CdX_2 system appeared in 1952 (6). It was found that the solubility of $CdBr_2$ was increased in tetrahydrofuran solvent by the addition of diethyl cadmium, indicating strong interaction and possibly redistribution. However, radioactive tracer studies, employing $Et_2{}^{115}Cd$ and $^{115}CdBr_2$, showed no exchange of the label after 21 days equilibration. When the complex was decomposed, the label was found either in the nonvolatile residue when $^{115}CdBr_2$ was used, or in the volatile residue when $Et_2{}^{115}Cd$ was used. Molecular weight data (not given) were claimed to support the formulation of the interaction as $Et_2Cd \cdot CdX_2$.

Later, a series of Russian papers appeared which reported confirmation of redistribution, in refutation of the paper cited above (6). It was reported (8) that mixtures of $(C_2H_5)_2Cd$ with $CdCl_2$, $CdBr_2$ and CdI_2 in diethyl ether produced a suspension of EtCdX (X = Cl,Br,I) which was isolated by filtration and characterized only by establishing the empirical formula, RCdX, by Cd analysis. The product (where X = Cl,I) was reported to react with benzoyl chloride to give ethylphenylketone in 46% yield. Also, it was reported that a compound of the empirical formula, C_4H_9CdBr, had been crystallized from ether. An equimolar mixture of R_2Cd (R = ethyl, n-butyl) and CdX_2 (X = Cl, Br,I) was reported (7) to precipitate a compound of the empirical formula, RCdX·diox, when 1,4-dioxane was added to the reaction mixture. The isolation of C_6H_5CdI was reported (10) from an equimolar mixture of

diphenylcadmium and cadmium iodide in diethyl ether. Characterization of this product was by cadmium and iodine analysis alone. It is important to note that these reported compounds were identified by a scheme which establishes the empirical formula $(RCdX)_n$ but does not give the value of n. Thus, when n = 2, $(RCdX)_2$ and $(R_2Cd \cdot CdX_2)$ both satisfy the same empirical formula.

In an attempt to resolve this ambiguity (11), n-BuCdI and EtCdI were allowed to react with EtMgCl and n-BuMgBr, respectively, in ether. As indicated in reactions (2) and (3), the proposed compound RCdX would give rise to an unsymmetrical compound RCdR', whereas the unredistributed species $R_2Cd \cdot CdX_2$ would react to produce a mixture of the symmetrical and unsymmetrical dialkyls.

$$RCdX + R'MgX \rightarrow RCdR' + MgX_2 \qquad (2)$$

$$\frac{1}{2} R_2Cd \cdot CdX_2 + R'MgX \rightarrow \frac{1}{2} R_2Cd + \frac{1}{2} R'_2Cd + MgX_2 \qquad (3)$$

Since the unsymmetrical dialkyl was isolated in 66 per cent yield by distillation from the salt-containing mixture, Kocheshkov, *et al.*, concluded that RCdX was the predominant reacting species. Another possibility which was not considered was that the magnesium salts in the mixture had catalyzed the formation of the unsymmetrical dialkyl from the symmetrical compounds according to Equation 4.

$$R_2Cd + R'_2Cd \xrightarrow{MgX_2} 2RCdR' \qquad (4)$$

Thus, the results of this experiment are not conclusive. The properties of the unsymmetrical dialkyls prepared by this method have been reported (13).

A paper dealing more extensively with the interaction between dialkyl cadmium and cadmium halide in ether appeared in 1967 (12). The syntheses of RCdX species (R = ethyl,n-propyl,n-butyl,phenyl; X = Cl, Br,I) were reported from the reaction of the corresponding cadmium dialkyls (aryl) and cadmium halides in diethyl ether. The yields of RCdX product varied from 25 per cent to 84 per cent. For R = ethyl, phenyl, the RCdX species were insoluble in the "usual" organic solvents. For R = n-propyl, n-butyl, however, the products were soluble in diethyl ether. The solubilities of all of the alkyl products were high in dimethyl sulfoxide (DMSO) and cryoscopic molecular weights in that solvent indicated species with an average molecular weight corresponding to the RCdX monomer unit. However, no consideration was given to the fact that this result is consistent with dissolved R_2Cd and CdX_2 alone. This is an important factor since dimethyl sulfoxide is an extremely good solvent for both R_2Cd and CdX_2. In the absence of other independent evidence for the composition of the soluble species, the molecular weight data alone are insufficient to identify an RCdX species in a mixture of R_2Cd and CdX_2.

As an extension of the work above (12), infrared data for the compounds $(C_2H_5)_2Cd$, C_2H_5CdBr, C_2H_5CdCl, and C_2H_5CdI have been published (14) and the data appear in Table 1, along with qualitative band assignments. Low solubility of the RCdX compounds prohibited obtaining the Raman spectra. The shift of the Cd-C stretching

Table 1

Compound	cm^{-1}	Intensity	Assignment
Et_2Cd	440	m	ν_s (Cd-C) stretch
	495	vs	ν_{as} (Cd-C) stretch
EtCdCl	474	s	(Cd-C) stretch
EtCdBr	470	s	(Cd-C) stretch
EtCdI	465	m	(Cd-C) stretch

frequency to lower energy was attributed to the effect of replacing one ethyl group of Et_2Cd with halogen. This shift could also be explained by simple coordination of CdX_2 by R_2Cd to give a species $R_2Cd \cdot CdX_2$ in which the Cd-C stretching frequency might also be altered.

In summary, empirical formulae, molecular weight data, and spectroscopic measurements are all consistent with the formulation $R_2Cd \cdot CdX_2$ as well as RCdX for these examples, both in solution and in the solid state.

Closely related to the redistribution problem is the unknown constitution of the "organocadmium reagent," which is used commonly in organic synthesis (15,16,17) for the conversion of acid halides to ketones. The reagent, generated by adding two moles of Grignard reagent to one mole of cadmium halide is represented by Equation (5), which is the familiar description of the species involved.

$$2\ RMgX + CdX_2 \rightarrow R_2Cd + 2\ MgX_2 \qquad (5)$$

The organocadmium reagent, in general, is less reactive toward ketones than the Grignard reagent. For some time it was assumed that the difference in alkylating ability of these two reagents was simply the difference in reactivity between RMgX and R_2Cd, R_2Cd being reactive toward acid chlorides, but relatively inert toward ketones.

Subsequent work (18) has proven this interpretation to be an oversimplification. Kollonitsch has shown that pure dialkylcadmium compounds react either sluggishly with acid halides to produce ketones in low yields or do not react at all. However, the addition of a quantity of lithium halide or magnesium halide results in a marked increase in the ketone yield. The activation of the reagent by metal salts occurs to the greatest extent when R_2Cd/MgX_2(or LiX) ≤ 1. The order of increasing activating ability, according to ketone yield, is $MgI_2 > MgBr_2 >> MgCl_2$. No information concerning the specific role of the metal salts was obtained.

Henry-Basch (19), *et al.*, also have compared the reactivity of pure dialkylcadmium compounds and the "usual organocadmium reagent" ($2RMgX + CdX_2$) toward acid chlorides, ketones, an alcohol, and aldehydes. Only for acetyl chloride and for n-pentanol were there more than traces of the expected product from reaction with the pure dialkylcadmium compound in boiling diethyl ether. The usual organocadmium reagent produced dramatic increases in the yields in all cases. Further, it was found (20) that the addition of metal halides to the pure dialkylcadmium compound, in an amount which is the same as that found for the "usual organocadmium reagents," resulted in yields which were identical to those of the reagents when allowed to react with

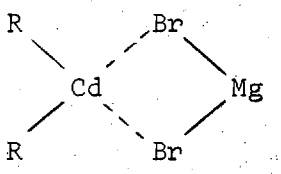
various acid chlorides, aldehydes, and ketones. The stoichiometry of the *in situ* or "organocadmium" reagents is indicated by Equations (6) and (7).

$$2(RX+Mg \rightarrow RMgX) + CdX_2 \rightarrow R_2Cd + 2MgX_2 \quad (6)$$

$$2(RX+2Li \rightarrow RLi+LiX) + CdX_2 \rightarrow R_2Cd + 4LiX \quad (7)$$

It was found (21) that reaction of one mole of a Grignard reagent (R = ethyl,n-propyl,n-butyl,n-pentyl) and one mole of $CdBr_2$ resulted in solution of the insoluble $CdBr_2$. Cooling of this solution yielded crystals of the empirical formula $RCdBr \cdot MgBr_2$ which exhibit the same reactivity (by yield) as the *in situ* reagent.

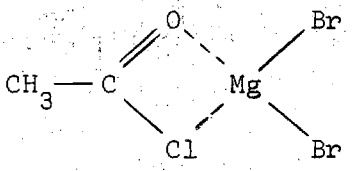
Comparison of the infrared spectra of the *in situ* reagent with a corresponding mixture of the pure dialkylcadmium compound and magnesium halides showed that the two are identical (22). The single difference observed in the infrared spectrum of the pure dialkylcadmium compound in diethyl ether when compared to the spectrum of the mixture of the dialkyl cadmium compound with MgBr, was the appearance of a band at 552 cm^{-1}. This absorption was invariant with different alkyl groups (methyl, ethyl, n-butyl) and was attributed to a vibration associated with the doubly halogen-bridged structure (I). It is curious that the bands associated with



(I)

the R_2Cd species were unaffected by the severe distortion from sp hybridization, normally assumed for these compounds, to the sp^3 geometry required by structure (I).

Recent French work (35) has described the formation of a covalent complex between CH_3COCl and $MgBr_2$ which is formulated as:



Evidence for this species was a shift in the frequency of the carbonyl chromophore when $MgBr_2$ was added. This complex was offered as an explanation of the manner in which magnesium halides activate acid halides for reaction with dialkyl cadmium compounds.

A kinetic study of the reaction between dibutyl cadmium and acyl halides has been carried out (36). The influence of halogen, solvent, and substituent were studied. The reaction was found to be first order in dialkyl cadmium and first order in acid halide, and a mechanism was proposed.

Finally, the preparation of organocadmium compounds directly from cadmium metal and an alkyl halide has been recently reported (23,24). Although cadmium did not react directly with alkyl halides

in the presence of solvents such as diethyl ether, tetrahydrofuran and benzene, the reaction did proceed in dimethyl sulfoxide, hexamethylphosphoramide, and dimethyl formamide (DMSO, HMPT, DMF) at temperatures below 0°C. In HMPT the reaction was described by Equation (8), where R = ethyl, n-propyl, n-butyl. The dialkylcadmium compound as the bis HMPT solvate was separated by direct distillation from the cadmium

$$2RI + 2Cd \xrightarrow[Et_2O]{HMPT} R_2Cd\ 2HMPT + CdI_2 \cdot 2HMPT \qquad (8)$$

halide and alkylated acyl halides in yields of ca. 40-50 per cent. No infrared spectra of the reaction products were presented; however, $CdX_2 \cdot HMPT$ was identified by comparison of its infrared spectrum with that of a prepared sample. The compound $CdBr_2 \cdot (DMSO)_4$ was isolated when the reaction was carried out in DMSO/THF. The results of these studies imply that a mixture of R_2Cd and CdX_2 was formed in DMSO, in contrast to the conclusion from molecular weight data (12) that RCdX species were predominant.

Thus, it is clear that an unambiguous description of the organocadmium reagent is far from complete. It is established that halides "activate" the reagent, but it has not been established if this is the result of the metal halide being associated with the organocadmium species or if the metal halide functions solely as an independent Lewis acid by interacting with the acyl halides, rendering them more susceptible to attack by the organocadmium compound.

Purpose

This study is concerned primarily with the composition of the *in situ* reagent. We are interested in what species are present in solution and in any interactions among these species. Compounds, such as RCdX, $R_2Cd \cdot CdX_2$ are directly related to the composition of the *in situ* reagents since they may be present as intermediates, or they may be present in larger quantities by virtue of equilibria, such as (9), (10), (11). Therefore, the redistribution problem has a direct bearing on the understanding of the behavior of the synthetic reagents.

CHAPTER II

EXPERIMENTAL AND INSTRUMENTATION

Reagents

Anhydrous diethyl ether was distilled from $LiAlH_4$ in a nitrogen atmosphere. Cyclohexane, benzene, 1,4-dioxane, and N,N,N',N'-tetramethylethylenediamine (TMED) were distilled at atmospheric pressure from $NaAlH_4$. All solvents were high-purity reagent grade, except hexane which was washed with concentrated H_2SO_4, and water, dried over Linde 4A molecular sieve, and distilled before use.

Magnesium was triply sublimed bulk metal (Dow Chemical Co.) and was machined into small chips, washed thoroughly with anhydrous ether, and dried at reduced pressure before use. Alkyl halides ($n\text{-}C_3H_7Cl$, $n\text{-}C_4H_9Cl$, $n\text{-}C_4H_9I$) were Eastman reagent grade and were distilled through a one foot packed column before use. After passage through molecular sieve-KOH columns, methyl chloride was condensed from the gas phase using a dry ice cold finger above the reaction medium. Cadmium chloride and iodide were used without purification after drying at reduced pressure (115°C) for at least two hours.

Analytical

Halogen analysis was accomplished titrimetrically using the standard Volhard procedure. Cadmium and magnesium were determined complexometrically using EDTA at pH 10, with Eriochrome Black T as the indicator. When magnesium and cadmium were present simultaneously, the

total metal content was determined by adding excess EDTA and back titrating with standard Mg^{2+}. Potassium cyanide was then added, masking the Cd^{2+} by forming the cyano complex and releasing an equivalent amount of EDTA corresponding to the amount of cadmium present, which was then determined by titration again with standard Mg^{2+}. The magnesium content was found by subtracting the cadmium equivalent from the total.

Spectroscopic Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 621 grating infrared spectrometer. Windows for solution cells and mull cells were CsI to enable acquisition of spectra from 1600 cm^{-1} to 200 cm^{-1}. For spectra of gaseous samples, a gas cell was constructed with NaCl windows, glass-NaCl O-ring seals, and a teflon needle valve with an O-ring joint for attachment to the vacuum line. The gas cell was approximately 10 cm in path length and could be evacuated to 10^{-5} mm.

Nmr spectra were recorded on a Varian Associates A-60 nuclear magnetic resonance spectrometer (60 Hz). Benzene and TMS were used as internal references.

Sample cells were flushed with nitrogen prior to use and were filled in the dry box or against a countercurrent stream of dry nitrogen.

Molecular Weight Measurements

Three methods were used. The first was the ebullioscopic method in diethyl ether, developed by Walker (25).

The second method involved measurement of the vapor pressure depression of a solvent containing an ideal solute. The organocadmium compounds, being weakly acidic and having minimal solvent-solute interactions, should be amenable to this procedure. The method utilized dual tensimeters in conjunction with a standard vacuum line as outlined by Shriver (26).

Figure 1 illustrates the components of the experimental setup which were used. (A) is a sealed-off reference solvent manometer with solvent reservoir (a). This manometer is filled and evacuated through a side arm (b). (B) is the sample manometer, connected to the sample and to the vacuum line by 18/9 O-ring joints (d). A high vacuum stopcock (e) isolates the sample from the mercury in the manometer arm during degassing. (C) is the sample tube and adapter. The unit is disassembled in the dry box and the sample tube (g) is loaded with solution. Then the tube is capped with the adapter which incorporates a Fisher-Porter, 4 mm, glass needle valve with Teflon stem. The unit is attached to the sample manometer (d) and the air volume is pumped out before degassing. After degassing three times, both the reference manometer reservoir and the sample tube are immersed in a water-filled dewar at 20-25°C. The pressures are read to ± 0.5 mm with a standard cathetometer, after temperature equilibrium is reached (about 30 minutes). The sample may be stirred using the small magnetic dasher (glass with metal core) in the sample tube (g). After the pressure measurements are complete, the needle valve is closed and the sample tube-adapter weighed. Hydrolysis of the sample tube contents followed by analysis gives the number of millimoles of solute, and the assembly

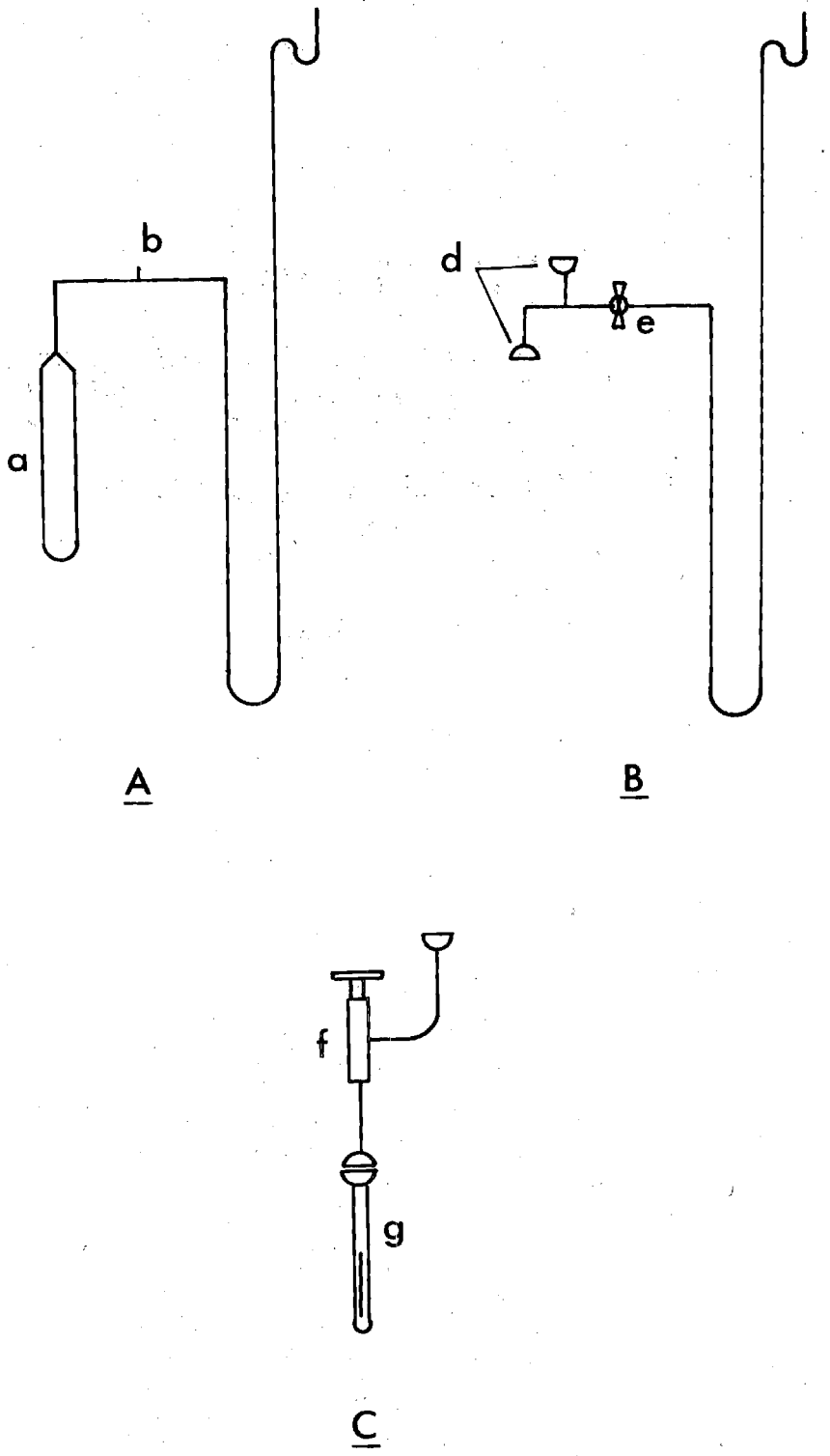


Figure 1. Components of Vapor Pressure Depression Molecular Weight Apparatus

weighed again empty to obtain the net weight of the tube contents. Grams of solvent = (net weight) - (grams of solute). Alternatively, solid sample may be introduced into the tared sample tube-adapter and solvent distilled onto the sample from a tared solvent bulb. In this case, correction for the weight of the solvent vapor in the manometer volume must be made.

Cryoscopy was the third method chosen for molecular weight measurements. Since diethyl ether does not freeze, cyclohexane was chosen as a solvent of convenient freezing point (6.5°C) and high cryoscopic constant (20.0, 20.30). Since it had been noted in earlier experiments that $(n\text{-}C_4H_9)_2Cd$ is miscible with non-polar solvents and that the redistribution product between $(n\text{-}C_4H_9)_2Cd$ and $CdCl_2$ was hydrocarbon-soluble, it was anticipated that some useful information could be obtained by cryoscopic methods in cyclohexane.

The apparatus which was fabricated is diagrammed in cross-section in Figure 2. The body of the container was constructed from inner and outer 45/50 standard taper ground glass joints, with the inner joint forming the bottom of the apparatus. A port (n) was provided for an inert gas purge and evacuation. After thoroughly drying the apparatus by repeated evacuation and nitrogen flush, solvent was introduced through a rubber septum (s) using a tared syringe. Sample solutions were injected likewise. The temperature was monitored as a function of time using a Beckmann differential thermometer (b) with a 19/38 standard-taper, ground-glass connection. Stirring was accomplished by a glass helix (h), surrounding the thermometer bulb. The stirring helix was driven up and down by an external, mechanically

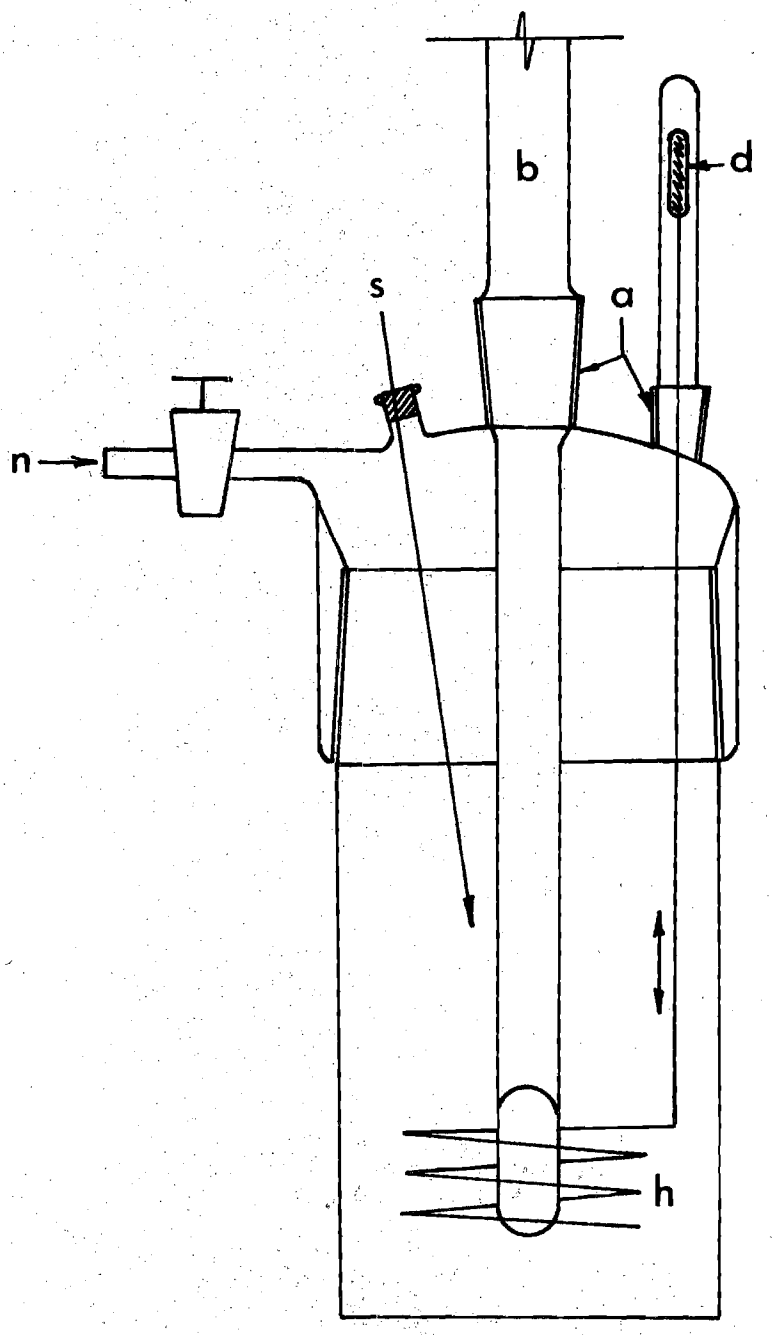


Figure 2. Cryoscopic Molecular Weight Apparatus

driven magnet which acted on a small glass-enclosed iron core (d) fused to the helix stem. Variable-speed, constant-rate stirring was thus accomplished in the isolated measuring apparatus volume.

Cooling curves were recorded (T vs. time) for pure solvent, and as portions of solute were added, with a constant stirring rate. Graphical treatment of the data yielded the freezing point depression for a given weight of solute. Apparent molalities were calculated using the formula, $m = T_f/K_f$, where m is the observed molal concentration, T_f is the freezing point depression in degrees, and K_f is the molal freezing point depression constant. Conditions of low concentration (ca. 0.05 m), the absence of strong solute-solvent interactions, and dissimilarity of solute and solvent geometries prohibiting solid solution formation, preclude special treatment of the data. Standardization of the technique, using triethylaluminum as a solute, yielded an i-value (apparent molecular weight/formula weight) of 1.97 in cyclohexane.

Preparative Methods

Magnesium Halides

The halides of magnesium were prepared by adding mercuric halide (previously dried at reduced pressure at 110°C for several hours) to an excess of magnesium suspended in an ether solvent (1). The reaction begins at once and was exothermic (condenser required). After stirring for 24 hours the Hg(II) was quantitatively reduced to elemental mercury and MgX_2 was dissolved in the ether. If the saturation concentration of MgX_2 ($MgBr_2 \cong 0.14$ M, MgI ≅ 0.26 M in diethyl ether at 25°C) was

exceeded, a two phase system resulted. The upper phase which was the bulk of the solution was simply a saturated ethereal solution. The lower phase was MgX_2 etherate and was fluid or crystalline since the melting point of this phase in the presence of excess ether was approximately at room temperature. The product solution at this point was clear and colorless and contained a dark gray residue of unreacted magnesium and finely divided elemental mercury. It may be stored indefinitely in this condition if tightly stoppered. Prior to use the solution was easily filtered to give a clear, colorless solution which was free of Hg(II). Mg:X = 1.0:2.0.

Grignard Reagents

Grignard reagents were prepared by adding an alkyl halide (neat or in an ether solution) dropwise to a stirred excess of magnesium in diethyl ether. The reaction was exothermic and the halide was added slowly in order to minimize side reactions and loss of solvent. The reactions required no initiation other than slight warming in some cases. Completely dry reagents and apparatus seemed to be the single best initiator. The products were clear, colorless solutions above a gray residue of unreacted Mg. These solutions were stable indefinitely if stoppered well, with the exception CH_3MgCl which disproportionated to produce $MgCl_2$ (insoluble in diethyl ether). Elemental analysis of these reagents indicated a Mg:X ratio which was 1:1 in all cases.

Preparation of $(CH_3)_2Cd$

To a slurry of 0.5 moles of anhydrous $CdCl_2$ in diethyl ether was added 0.99 moles of methyl magnesium chloride in 1.8 l. of dry ether.

The reaction was exothermic, requiring a dry ice condenser, and a large increase in reaction mixture volume was noted. After Grignard reagent addition was complete, the thick mixture was stirred for 18 hours, then filtered, and the insoluble residue washed well with 0.5 l. of dry ether. The residue was discarded. The solvent was removed from the ethereal solution of $(CH_3)_2Cd$ by vacuum distillation. The final stage of solvent removal was accomplished at atmospheric pressure by conventional distillation procedures in an atmosphere of dry nitrogen. The head temperature of the apparatus rose from 35°C to 103°C. Final purification was accomplished by distillation at reduced pressure (1-5 mm) at 33-45°C, yielding a colorless liquid product which was stored frozen in dry ice as a mass of white crystals.

Infrared examination of the product showed a sharp absorption at 520 cm^{-1} and a broad band at 675 cm^{-1}. A trace of ether was evident also.

Preparation of $(n\text{-}C_3H_7)_2Cd$

To a stirred suspension of anhydrous $CdCl_2$ (0.226 mole) in diethyl ether was added propyl magnesium chloride (0.453 moles). The thick reaction mixture was stirred for three hours. Filtration of the mixture, followed by thorough washing produced a clear, colorless solution of the dialkyl cadmium compound. However, on attempted isolation of the product by distillation at reduced pressure (5 mm, 65°C), decomposition took place to produce hydrocarbon and metallic cadmium.

$(n\text{-}C_4H_9)_2Cd$

Two moles of a standardized solution of Grignard reagent were added dropwise to one mole of $CdCl_2$ suspended in diethyl ether.

The $CdCl_2$ suspension was cooled in dry ice as the addition was made and the reaction vessel was protected from light with aluminum foil. After the addition was complete, the reaction vessel was allowed to warm to room temperature with continual stirring. The product mixture was a white or light gray suspension of $MgCl_2$ in a clear colorless solution of n-Bu_2Cd. Exposure of this mixture to light caused darkening of the solid in the mixture, presumably due to decomposition of the dialkyl cadmium compound to hydrocarbon and black, metallic cadmium. The solution containing the product was separated from the by-product $MgCl_2$ by filtration, followed by washing. The clear, colorless filtrate (which contains some magnesium halide) may be stored in the refrigerator without further degradation (some $MgCl_2$ may precipitate).

Isolation of the dialkyl cadmium compound was accomplished by first reducing the volume of the solution by reduced pressure distillation. The concentrate was then fractionated at reduced pressure to remove the ether which remains tenaciously attached to the magnesium salts which are present. n-Bu_2Cd was recovered last at a pressure of 0.5 mm and a pot temperature of 80-85°C. The product was a clear, colorless liquid which was frozen to a white crystalline solid as it dripped into a receiver cooled in dry ice or liquid nitrogen. A short-path molecular still was designed for this final purification step and is diagrammed in Figure 3.

This all-glass distillation apparatus was designed to permit effective purification of the dialkyl cadmium product while minimizing: (a) the length of the distillation path, (b) the resultant decomposition, and (c) contamination by stopcock grease. An oil bath (o)

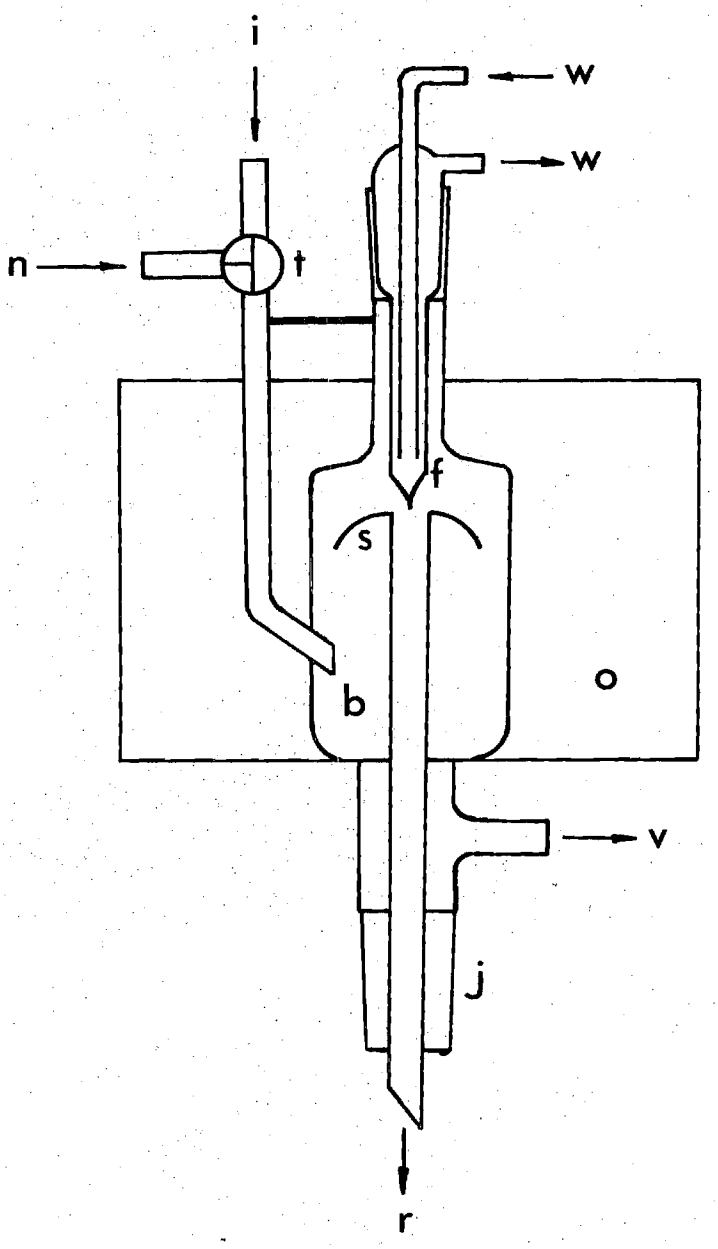


Figure 3. Short-path Distillation Apparatus for Purification of Organocadmium Compounds

surrounded the distillation flask (b) and was heated with an immersed coil of nichrome wire. The distillation flask was filled via syringe (i) through a three-way, 2mm stopcock (t) counter to a dry nitrogen flush maintained through (n). The shield (s) deflected any impure pot residue which bumped in the direction of the water-cooled (w) cold finger (f). The product condensed on the cold finger and dripped directly into a receiver (r) connected to the apparatus by a standard taper ground glass joint (j). The receiver was conveniently cooled in dry ice or liquid nitrogen. Evacuation of the assembly was accomplished through (v).

Attempted purification of n-Bu_2Cd on the vacuum line resulted in negligible transfer after eight hours (not heated). Some attack of the cadmium compound on the silicone stopcock grease in the system did occur. The precipitation of magnesium salts in the final purification step complicated the distillation and caused worrisome bumping. The use of 1,4-dioxane to remove these salts prior to the final distillation is suggested.

Gravimetric analysis of the pure liquid n-Bu_2Cd indicated a purity of 98.7 per cent by cadmium analysis. An infrared spectrum of the neat liquid (Figure 4) indicated no residual ether. An nmr spectrum of the product indicated the triplet associated with the α-methylene protons to be 401 cps upfield from an internal benzene standard in diethyl ether solution (vs. 249 cps for α-CH_2 in n-BuI). The remainder of the spectrum consisted of a triplet due to the terminal methyl and a complex multiplet composed of a quintet and a sextet arising from the β and γ methylene protons.

Di-n-butyl cadmium is stable when stored frozen or in the refrigerator protected from light. If the compound is exposed to light or warmed to room temperature, obvious darkening occurs. For this reason, transfers were made in the dark and/or in the cold where possible.

$(CH_3)_2Cd + CdCl_2$ in Diethyl Ether

33.4 moles of dimethyl cadmium and 33.4 mmoles anhydrous $CdCl_2$ were combined in 50 ml of diethyl ether. The volume of insoluble material increased by a factor of two and there was no noticeable heat of reaction. After stirring for 18 h. the mixture was filtered and the filtrate and residue were examined by infrared spectroscopy. The spectrum of the soluble portion of the redistribution mixture was compared with an identical solution of dimethyl cadmium containing no $CdCl_2$. The bands arising from $(CH_3)_2Cd$ at 520 cm^{-1} and 670 cm^{-1} in the $(CH_3)_2Cd$-$CdCl_2$ mixture were dramatically reduced in intensity from the bands in the control solution. However, no additional bands were observed which could be attributed to a soluble interaction product. The spectrum of the solid residue from the redistribution exhibited only a single broad absorption at ca. 680 cm^{-1}. It was concluded that interaction had occurred to yield an insoluble product. Since a soluble product was desired for spectral study and composition measurements, this product was not investigated further.

$(n\text{-}C_4H_9)_2Cd$ + $CdCl_2$ or CdI_2 in Diethyl Ether

Anhydrous cadmium halides were suspended in a quantity of diethyl ether and an equimolar amount of neat $(n\text{-}C_4H_9)_2Cd$ was then added at once with a syringe or pipette. The flask was covered and the mixture

was stirred continuously at room temperature. No apparent heat of reaction resulted. Alternatively, a standard solution of the dialkyl cadmium compound in diethyl ether may be added to the cadmium halide suspension.

In a typical experiment, 57 mmoles of n-Bu_2Cd were added to 57 mmoles of $CdCl_2$ in approximately 150 ml of diethyl ether. After 96 hours the supernatant solution had the elemental ratio Cd:Cl = 1.2:1.0 and a cadmium molarity of 0.5. Addition of excess $CdCl_2$ did not alter this ratio. The insoluble portion of the mixture contained cadmium and chloride in the ratio of 1.0:1.67. The molar ratio of the supernatant solution indicates that the interaction is not completely in favor of the product (K = 5).

Combination of 28 mmoles of n-Bu_2Cd and 28 mmoles of CdI_2 in 100 ml of diethyl ether, after 26 hours of stirring, produced a mixture whose soluble portion exhibited a cadmium to iodide ratio of 1.09:1.0 and whose insoluble portion gave the ratio 1.05:1.0. The molarity of soluble cadmium in this case was 0.35 M.

Cooling of the supernatant solutions in these two cases produced crystalline, white solids, isolated by filtration in the cold, which had the following analyses (n-Bu by difference): n-Bu:Cd:Cl = 1.1:1.04:1.0; n-Bu:Cd:I = 1.17:1.04:1.0. An attempt to redissolve these solids in ether resulted in apparent disproportionation giving insoluble CdI_2 (Cd:I = 1.0:1.8) and $CdCl_2$ (Cd:Cl = 1.0:1.6). The addition of TMED (tetramethylethylenediamine) to the supernatant of the n-Bu_2Cd-$CdCl_2$ redistribution reaction precipitated a solid in about two minutes with the empirical formula: Cd:Cl:TMED = 1.0:1.94:1.03. A similar

experiment for the CdI_2 system produced no precipitate after four hours of stirring.

$(n\text{-}C_4H_9)_2Cd + CdCl_2$ or CdI_2 in Cyclohexane

Stirring 17.14 mmoles of $(n\text{-}C_4H_9)_2Cd$ with 54.55 mmoles of $CdCl_2$ in 20 ml of dry cyclohexane for 72 hours at room temperature in the dark, produced a suspension of a light gray precipitate in a clear solution. The Cd:Cl ratio of the supernatant solution was 3.7:1.0, indicating incomplete interaction even in the presence of excess halide. Cooling of the supernatant portion of the reaction mixture produced a small amount of colorless, crystalline solid, identified by its infrared spectrum as being identical to the solid of empirical formula $n\text{-}C_4H_9CdCl$ obtained from the redistribution reactions in diethyl ether. The compound disproportionated when an attempt was made to dissolve it.

Similarly, 26.5 mmoles of $(n\text{-}C_4H_9)_2Cd$ and 41.64 mmoles of CdI_2 were combined in 20 ml of cyclohexane. After 48 hours of stirring, the precipitate volume in the reactor had doubled over the original halide volume and analysis of the supernatant solution indicated a cadmium concentration below 0.03 molar; i.e., interaction is essentially complete and the product is insoluble. The infrared spectrum of the solid portion of this reaction mixture was identical to the spectrum of the product with empirical formula C_4H_9CdI which was isolated from an equimolar mixture of $(n\text{-}C_4H_9)_2Cd$ and CdI_2 in diethyl ether.

$n\text{-}C_4H_9MgCl + CdCl_2$ (1:1) in Diethyl Ether

A portion of standardized Grignard solution was added dropwise to a stirred suspension of $CdCl_2$ in diethyl ether, cooled to dry ice

temperature. The reactor was protected from light by a covering of aluminum foil. After the addition was complete, the dry ice was allowed to evaporate and the reactor warmed slowly to room temperature with continual stirring. The product mixture consisted of a white solid suspended in a clear, colorless solution. The mixture darkened very slowly when stored protected from light at room temperature; however, rapid discoloration (gray) occurred when the mixture was left exposed to room light.

Elemental analysis of the supernatant solution indicated the following ratios: Mg:Cd:Cl = 1.0:1.81:3.36, Cd:Cl(-$MgCl_2$) = 1.33:1.0. These ratios were constant within ± 0.1 after stirring for one week. A Gilman test was negative for both supernatant and precipitate, indicating that the Grignard was completely consumed. The concentrations of the species present in the supernatant were as follows: M_{Cd} = 0.093 (82% total Cd), M_{Mg} = 0.052 (46% total Mg), M_{Cl} = 0.17 (50% total Cl).

The insoluble portion of the reaction mixture yielded elemental ratios as follows: Mg:Cd:Cl = 2.19:1.0:5.88, Cd:Cl(-$MgCl_2$) = 1.0:1.50. Cadmium species accounted for 31 per cent of the insoluble portion.

Fractional crystallization of the supernatant of the (1:1) reaction by adding petroleum ether and removing solvent at reduced pressure produced white solids which had the following elemental ratios: first fraction-Mg:Cd:Cl = 1.01:1.0:3.57, second fraction-Mg:Cd:Cl = 2.45:1.0:4.08, remainder-Mg:Cd:Cl = 1.0:9.94:9.35. Cooling of the supernatant in dry ice produced a slowly forming precipitate which, when isolated by filtration in the cold, gave the analysis:

Mg:Cd:Cl = 1.0:1.06:2.98. The addition of TMED to a sample of the supernatant produced a white solid having the analysis: Mg:Cd:Cl = 1.0:1.7:3.99, Cd:Cl(-$MgCl_2$) = 1.0:1.17. The filtrate from this precipitation gave the analysis: Mg:Cd:Cl = 1.0:2.0:2.76, Cd:Cl = 2.86:1.0.

n-C_4H_9MgCl + $CdCl_2$ (2:1) in Diethyl Ether

The addition of the Grignard reagent was made according to the procedure outlined for the (1:1) reaction. Again, the product was a white solid suspended in a clear, colorless solution. Exposure of the product mixture to light induced darkening of the product. Gilman tests were negative for both soluble and insoluble fractions of the product.

In a reaction between 30.6 mmoles of n-BuMgCl and 15.3 mmoles of $CdCl_2$ in 240 ml of diethyl ether, the supernatant solution gave the following analysis: Mg:Cd:Cl = 1.0:3.71:2.14, Cd:Cl(-$MgCl_2$) = 26.5:1.0. M_{Cd} = 0.070 (100% total Cd), M_{Mg} = 0.019 (15% total Mg), M_{Cl} = 0.041 (16% total Cl). The insoluble portion of the reaction mixture gave the analysis; Mg:Cd:Cl = 78.7:1.0:152.7, Mg:Cl = 1.0:1.93. Calculated for $MgCl_2 \cdot Et_2O$: (Mg, 14.35%; Cl, 41.8%). Found: (Mg, 14.5%; Cl, 41%).

n-C_4H_9MgI + CdI_2 (1:1) in Diethyl Ether

The addition procedure is outlined above for the (1:1) and (2:1) chloride analogs. The reaction between 88 mmoles of n-BuMgI and 88 mmoles of CdI_2 in 1000 ml of diethyl ether, after 24 hours of stirring, protected from light, produced a mixture consisting of a light gray solid suspended in a clear, colorless supernatant solution. Analysis

of the supernatant solution gave the elemental ratios: Mg:Cd:Cl = 1.28:1.0:2.99, Cd:I(-MgI_2) = 2.32:1.0. M_{Mg} = 0.081 (98% total Mg), M_{Cd} = 0.063 (71% total Cd), M_I = 0.19 (72% total I). The residue from filtering the reaction mixture was very photosensitive and turned black at the surface in spite of precautions to keep it well covered. Analysis of this solid produced the ratios: Mg:Cd:I = 1.0:1.70:5.04, Cd:I(-MgI_2) = 1.0:1.79. A Gilman test was negative for both supernatant and residue from this reaction. This reaction was performed under conditions such that the solubility limit of MgI_2 would not be exceeded (ca. 0.26M).

Upon standing at room temperature for periods greater than one week, colorless crystals grew on the sides of the flask containing the (1:1) supernatant solution. Analysis indicated a composition of: Mg:Cd:I = 1.41:1.0:4.10, Cd:I(-MgI_2) = 1.0:1.28.

Fractional crystallization of the (1:1) supernatant was performed by adding dry hexane and boiling off the solvent. Initially, a photosensitive solid precipitated, which had the following composition: Mg:Cd:I = 1.28:1.0:3.92, Cd:I(-MgI_2) = 1.0:1.36. Further removal of ether resulted in the appearance of a two phase system. The lower phase gave the analysis: Mg:Cd:I = 2.46:1.0:5.05, Mg:I = 1.0:2.04. The upper phase was very dilute in Cd, Mg and I species and yielded the ratios: Mg:Cd:I = 1.31:3.31:1.0; the low value for I reflects the error in analysis for the high dilution. The lower phase was very small in volume in contrast to the large amount of upper phase (hexane). The lower phase was probably molten $MgI_2 \cdot nEt_2O$ containing some dissolved $(n\text{-}C_4H_9)_2Cd$.

Cooling of the (1:1) supernatant in dry ice initiated the slow precipitation of a white solid, isolated by filtration in the cold, which had the elemental ratio: Mg:Cd:I = 1.0:1.10:2.85, similar to the substance isolated from the analogous chloride system.

Tetrahydrofuran was added to a quantity of the (1:1) supernatant such that sufficient ligand would be available to form the very insoluble complex $MgI_2 \cdot 6THF$. An instantly-forming white precipitate appeared where the drops of THF entered the solution, which redissolved immediately. As the addition was completed, a permanent white precipitate was evident, along with a small pellet of semisolid material. Stirring for 12 h. followed by filtration produced a pure white precipitate with the analysis: Mg:Cd:I = 2.27:1.0:6.22, Cd:I(-MgI_2) = 1.0:1.68. Removal of solvent from the filtrate at reduced pressure produced additional precipitate with the elemental ratios: Mg:Cd:I = 4.35:1.0:9.32, Cd:I(-MgI_2) = 1.61:1.0. The remaining filtrate had the analysis: Mg:Cd:I = 1.86:7.36:1.0.

Removal of solvent from the (1:1) supernatant at reduced pressure resulted in the appearance of white solid which redissolved when the mixture was warmed to room temperature. The final product of solvent removal was a viscous, clear liquid which bubbled when exposed to air and crackled when poured into water.

<u>$n\text{-}C_4H_9MgI + CdI_2$ (2:1) in Diethyl Ether</u>

The mode of addition has been described above. A white precipitate was evident immediately after addition of the Grignard was complete; the precipitate dissolved completely after 40 hours of stirring, resulting in the formation of a homogeneous, clear, colorless solution.

A minute amount of black precipitate was observed after the solution was allowed to stand at room temperature for one week. Analysis of the solution resulting from the reaction between 44.1 mmoles of n-C_4H_9MgI and 22.06 mmoles of CdI_2 gave the following elemental ratios: Mg:Cd:I = 1.95:1.0:3.77, Mg:I = 1.0:1.93. M_{Mg} = 0.202. A Gilman test was negative for the reaction mixture.

Removal of solvent from the reaction mixture at reduced pressure initially produced a solid precipitate at the cool temperature generated by the evaporating solvent. This precipitate redissolved upon warming the mixture to room temperature. The ultimate product of solvent removal was a clear, viscous liquid which crackled loudly when poured into water and bubbled vigorously when exposed to air.

The addition of hexane to a sample of the (2:1) reaction mixture produced a colorless, two-phase system with no solid precipitate. Analysis of each phase yielded the following: Upper phase- Mg:Cd:I = 1.0:1.24:2.07, lower phase- Mg:Cd:I = 4.04:1.0:8.46. Removal of diethyl ether by distillation caused a slight increase in the volume of the lower layer. Again, analysis showed the following: Upper phase (very dilute)- Mg:Cd:I = 1.0:10.64:1.50, Lower phase- Mg:Cd:I = 3.65:1.0:7.61.

Cooling of a portion of the reaction mixture caused the precipitation of a large amount of white solid which gave the analysis: Mg:Cd:I = 3.66:1.0:7.84, Mg:I = 1.0:2.14.

The Gilman Test (27,28)

This is a widely used color test which detects the presence of organometallic reagents capable of alkylating Michler's Ketone, 4,4'-bis(N,N-dimethylamino)benzophenone.

A few drops of the solution to be tested, or a small amount of solid is added to 1 or 2 ml of a 1 per cent solution of Michler's Ketone in benzene. After mixing, 1 or 2 ml of distilled water is added, plus several drops of glacial acetic acid, containing a trace of I_2. A color is evident with reactive organometallic compounds.

In these experiments, the Grignard compounds gave a strong positive test (blue or blue-green colors in the aqueous and benzene phases). All of the Grignard:CdX_2 mixtures (1:1,2:1) and n-Bu_2Cd gave negative color tests, i.e., no color developed in comparison with blank tests.

CHAPTER III

RESULTS AND DISCUSSION

The equilibria represented by equations (9), (10) and (11), describe the relationships among the chemical species as defined by this work. The nature of the solvent is most important in the consideration of the equilibria since the solvation of the species present affects the solubility, association, and the position of the equilibria. Diethyl ether was chosen for use in this study because it is the solvent

$$\begin{array}{ccccccc} RMgX & + & CdX_2 & \rightarrow & RCdX & + & MgX_2 \rightleftarrows RCdX \cdot MgX_2 \\ & & & & \uparrow\downarrow & & \end{array} \qquad (9)$$

$$R_2Cd \cdot CdX_2 \rightleftarrows R_2Cd + CdX_2 \rightleftarrows 2RCdX \qquad (10)$$

$$2RMgX + CdX_2 \rightarrow R_2Cd + 2MgX_2 \rightleftarrows R_2Cd \cdot MgX_2 + MgX_2 \qquad (11)$$

used in the preparation of "organocadmium reagents."

The Lewis acidity of the metal atom in Group II organometallic compounds varies considerably with the different metals and, for a given member of the Group, is variable according to the substituents which are bound to the metal. For example, the substitution of an alkyl group in a dialkyl metal compound by a more electronegative halide atom would have the effect of increasing the acceptor power of the metal. Typical donor-acceptor processes, such as self-association

and coordination of donor molecules, will thus be influenced by these effects. It is found that the metals of Group IIA are, in general, stronger Lewis acids than those in Group IIB, in compounds having the same substituents.

The two metals involved in this study, magnesium and cadmium, exhibit just such a dichotomy of properties. A quantitative study of the behavior of organomagnesium (9) compounds with bound groups altered systematically has shown that the tendency of the compounds to participate in self-association, at comparable concentrations, increases in the order: $R_2Mg < RMgX < MgX_2$ (R = alkyl or aryl, X = halogen). This order is attributed to the effect of the halogen in withdrawing electron density from magnesium. Also, organomagnesium compounds strongly coordinate donor molecules such as ethers and amines. In contrast, organocadmium compounds demonstrate little affinity for donor molecules and do not associate to give polymeric forms. Dialkyl-and diarylcadmium compounds have been shown to be monomeric in cyclohexane, benzene, and 1,4-dioxane, by cryoscopic molecular weight measurements (29). Dimethyl cadmium will form crystalline 1:1 complexes with bifunctional donors, such as 1,4-dioxane, 2,2'-bipyridyl, etc. (30,31,32), but complexes with monofunctional ligands dissociate on attempted isolation (32). Crystalline dioxanates of diarylcadmium species have been reported which lose dioxane readily on heating (80°C) (13). Also, stable complexes such as $R_2Cd\cdot(HMPT)_2$ have been isolated (24) (R = ethyl, n-propyl, n-butyl, HMPT = hexamethylphosphoramide). Essentially nothing is known about complexes of organocadmium halides and no solvates of RCdX have been isolated. In consideration of the trends observed for

organomagnesium compounds, a more pronounced affinity for donor molecules might be anticipated for "RCdX" as compared with R_2Cd. This contrast would be exhibited in the formation of complexes, association behavior, and solubility.

Consideration of the possibility of a special case of acid-base behavior as discussed above is important. The interaction between the magnesium halides produced in reactions 9 and 11 and the organocadmium species present in the mixture needs to be considered. It is the nature of this interaction, if any, which is important to the understanding of the role of magnesium halides in "activating" a pure dialkylcadmium species toward reaction with an acid halide. Important aspects of this mixture include competing acid-base equilibria involving interactions such as: solvent-MgX_2, MgX_2-MgX_2, MgX_2-RCdX, and MgX_2-R_2Cd.

Infrared Spectra

The region of the infrared spectrum utilized in most of this work includes the portion from 1600 cm^{-1} to 200 cm^{-1}. Absorption in this range occurs for the following: Carbon chain deformations, C-C stretch, C-O stretch, C-N stretch, C-metal (M) stretch for Group II organometallics, C-M-C deformation, and M-X stretch for MX_2. Potentially, this region would also include distinctive absorptions arising from donor molecules bound to organometallic species.

Inherent in the linear geometry of the simple cadmium dialkyls is a useful consequence of this unique symmetry. If rotation is rapid about the C-Cd bond, allowing $D_{\infty h}$ symmetry point group designation,

then of the four normal modes for this molecule (assuming a three-body molecule R-M-R), the symmetric C-Cd stretch (ν_s) will be Raman active only, and the asymmetric C-Cd stretch (ν_{as}) will be infrared active only. The degenerate deformation vibrations are infrared active. This mutual exclusion property will be relaxed if the symmetry is lowered from $D_{\infty h}$ by bending the molecule ($D_{\infty h} \rightarrow C_{2v}$), substituting another ligand for one alkyl group ($D_{\infty h} \rightarrow C_{\infty v}$ if linear, $D_{\infty h} \rightarrow C_s$ if non-linear), or if the alkyl skeleton is of such low symmetry that rapid rotation about the C-Cd bond will not preserve the assignment of $D_{\infty h}$ symmetry. For the mercury dialkyls (33), where R = ethyl, i-propyl, preservation of the exclusion principle is observed; however, if R = n-propyl, n-butyl, the symmetric and asymmetric C-Hg stretching vibrations are observed in both the Raman and the infrared. This behavior was attributed to the failure of free rotation to preserve the symmetry.

Dimethyl cadmium (34) exhibits an absorption band in the infrared at 538 cm^{-1}, assigned to the asymmetric CH_3-Cd stretching vibration and an absorption band in the Raman at 465 cm^{-1}, attributed to the symmetrical stretching vibration. The infrared spectrum of diethyl cadmium (14) is reported to have an absorption at 495 cm^{-1} (ν_{as}) and a second absorption at 440 cm^{-1} due to ν_s. No Raman data were presented and the assignment of ν_s is uncertain. Infrared data for EtCdCl, EtCdBr, and EtCdI in hydrocarbon solvent (14) yield values for the C-Cd stretch at 474, 470, and 465 cm^{-1}, respectively. The compounds were not soluble enough to obtain Raman spectra. French workers (22) have presented pictorially the spectrum of dimethyl-, diethyl-, and di-n-butyl-cadmium from 700 cm^{-1} to 450 cm^{-1} with no band assignment.

Figure 4 shows the infrared spectrum which we obtained for neat n-Bu_2Cd as a liquid film. Two strong absorption bands at 644 cm^{-1} and 501 cm^{-1} dominate the spectrum below 700 cm^{-1}. A tentative assignment may be made by assigning the 644 cm^{-1} band as the C-Cd asymmetric stretching vibration and the 501 cm^{-1} absorption as the symmetric stretching vibration, which is allowed in the infrared because of the low symmetry of the butyl group attached to cadmium. As expected, ν_s is of diminished intensity compared to ν_{as}. This assignment is analogous to the n-Bu_2Hg case, discussed above, where ν_s is at 519 cm^{-1} and ν_{as} is at 602 cm^{-1} in the infrared (Raman- ν_s at 505 and ν_{as} at 596). The spectrum of n-Bu_2Cd dissolved in diethyl ether is identical to a superposition of the two independent spectra, indicating no solute-solvent interaction.

Infrared spectra of nujol mulls of anhydrous $CdCl_2$ and CdI_2 show no absorption bands as low as 200 cm^{-1}. Spectra of the etherates of $MgCl_2$ and MgI_2, as nujol mulls, are rich in strong bands. The spectrum of $MgCl_2 \cdot Et_2O$ is shown in Figure 11 as the 2:1 solid product from the reaction of n-C_4H_9MgCl and $CdCl_2$ in diethyl ether. The infrared spectrum of $MgI_2 \cdot nEt_2O$ is seen in Figure 14. Clearly, most of the bands in these spectra are due to coordinated diethyl ether. The Mg-X stretch and MgX_2 deformation modes are expected at low energies (ca. 300 cm^{-1} and below) and assignment is not important for the halides. The halide spectra, both in solution and as solid ether solvates, have been recorded, and these spectra were used to confirm the presence of these compounds in product mixtures.

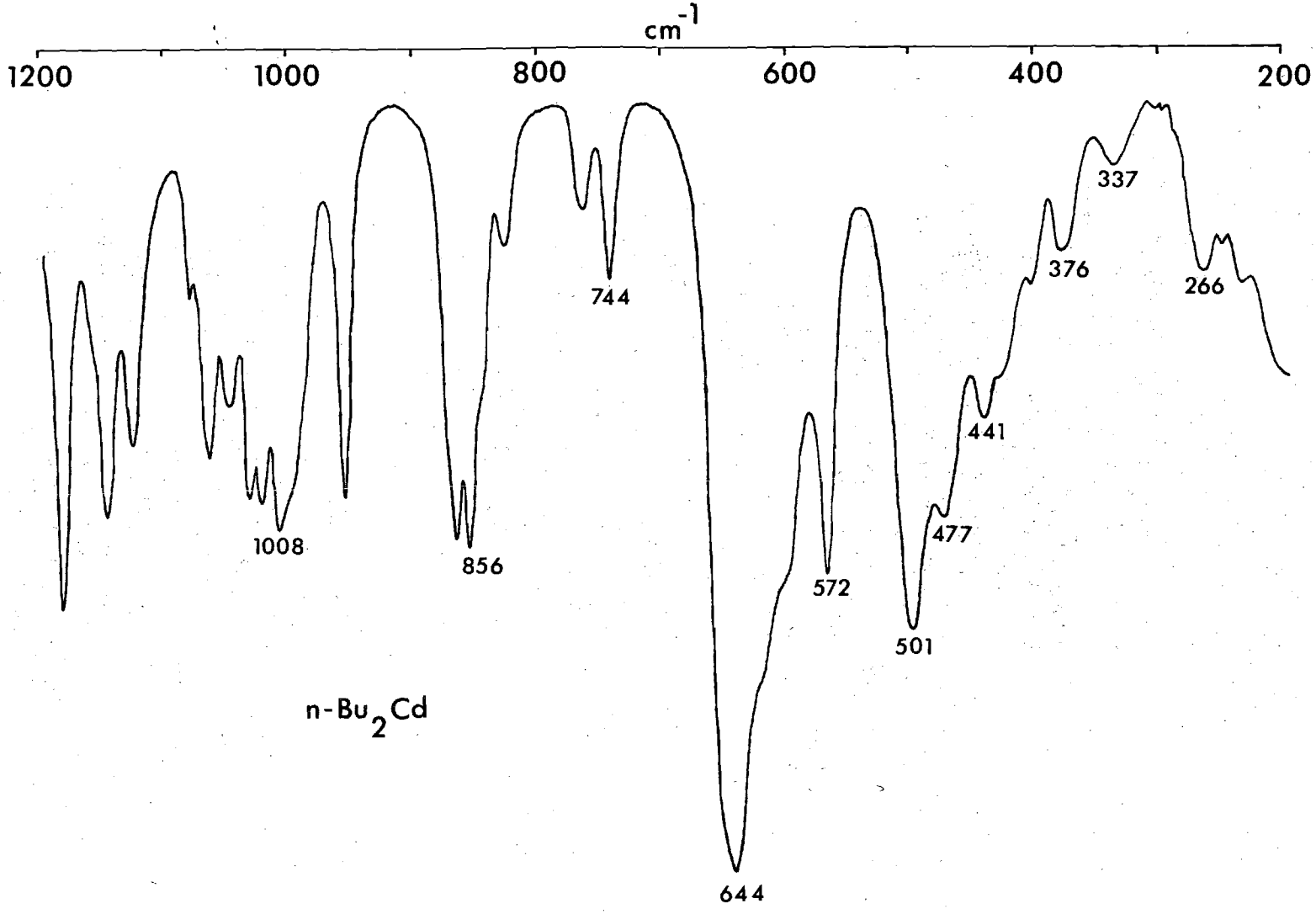


Figure 4. Infrared Spectrum: Neat $(n\text{-}C_4H_9)_2Cd$, Liquid Film

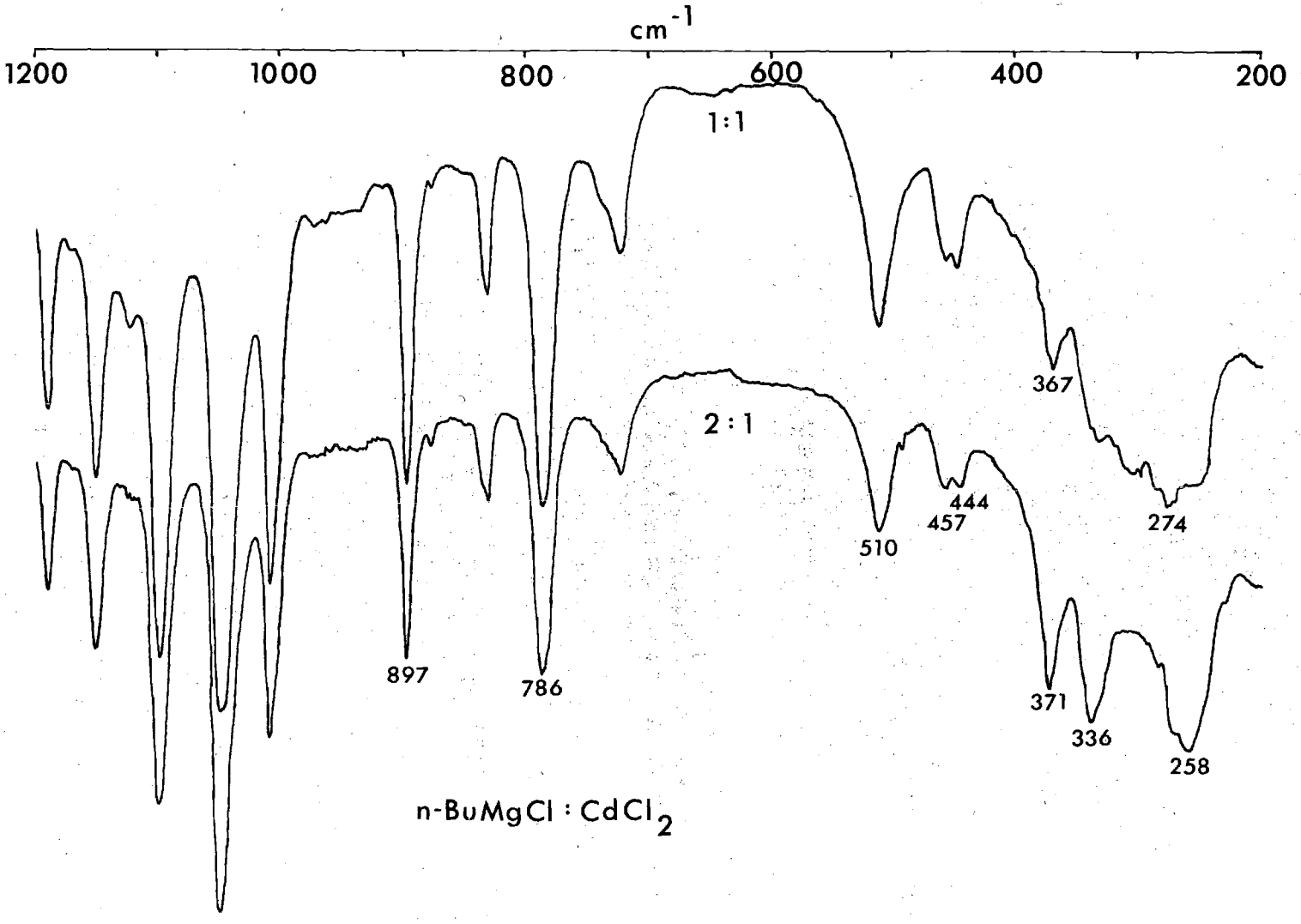


Figure 11. Infrared Spectrum: Insoluble Products from the Reaction of n-C_4H_9MgCl with $CdCl_2$ in Diethyl Ether. Lower Curve- Products from 2:1 Mixture; Upper Curve- Products from 1:1 Mixture

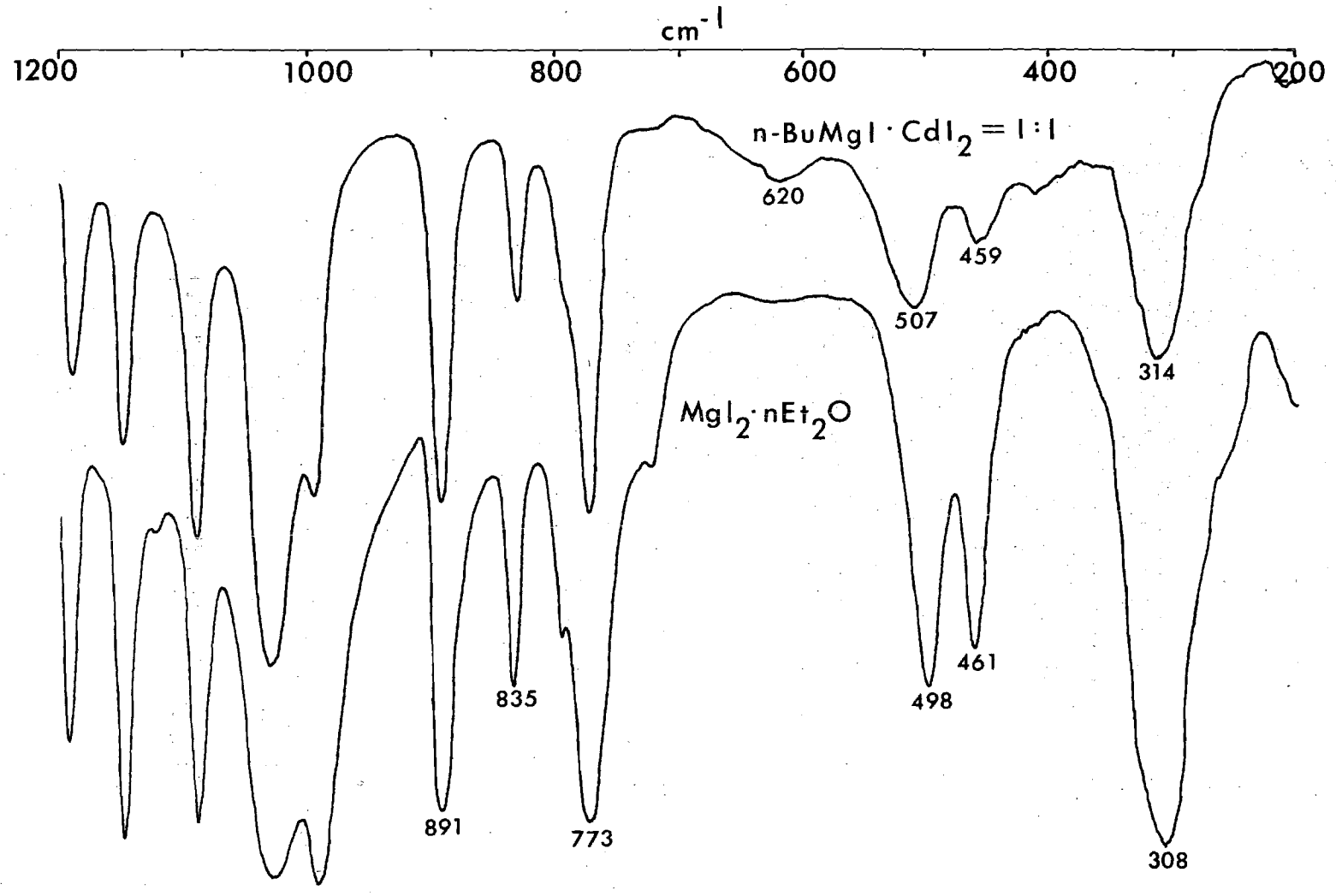


Figure 14. Infrared Spectrum: Upper Curve- Insoluble Product from the Reaction of n-C_4H_9MgI with CdI_2 in Diethyl Ether in 1:1 Ratio. Lower Curve- Magnesium Iodide Etherate

Molecular Weight Data

Three classical methods of molecular weight measurement were used in an attempt to demonstrate the composition of the organocadmium species and adducts in solution. Persistent anomalous behavior characterized many of the experiments which were performed.

Ebullioscopic measurements in diethyl ether were not successful when alkyl cadmium compounds were present, e.g., the i-values for $(n\text{-}C_4H_9)_2Cd$ ranged from 0.78 to 0.85 for concentrations of 0.012 to 0.032 molal. Increasing turbidity of the sample solutions during measurement, and the low i-values, indicated decomposition of the solute. This is not surprising since alkyl compounds are known to be somewhat metastable and prone to decompose under the influence of heat or light. In an environment of boiling solvent this situation would only be aggravated.

A second method, vapor pressure depression, was also attempted without success. Again, it was found for solutions of alkyl cadmium species that an equilibrium condition could not be established for measurement of vapor pressure over the test solutions. Instead, a slow, steady increase in apparent vapor pressure was observed. Examination of the vapor over the test solutions by infrared spectroscopy failed to indicate the presence of gases other than the solvent vapor (diethyl ether). It is possible that bands arising from a volatile decomposition product might be masked by the strong absorption bands of the solvent. This result precluded further measurements of alkyl cadmium compounds.

Measurement of freezing point depression in cyclohexane solvent was the third method used in this study. Solubility of the compounds to be studied was the limiting condition for this technique. An i-value of 0.99 was obtained for $(n\text{-}C_4H_9)_2Cd$, indicating that this compound is monomeric in cyclohexane (29) and that the dialkyl is stable under the conditions of measurement. Redistribution mixtures ($n\text{-}Bu_2Cd\text{-}CdCl_2$, CdI_2) were prepared in cyclohexane and the soluble portions examined by the cryoscopic method. The iodide system had no soluble products and could not be examined. However, good cooling curves were obtained for the chloride system before precipitation eventually occurred. Using the supernatant solution from the $(n\text{-}C_4H_9)_2Cd\text{-}CdCl_2$ mixture in cyclohexane (Cd:Cl = 3.17:1.0) as a test solution and assuming the excess $(n\text{-}C_4H_9)_2Cd$ to be monomeric, the apparent molecular weight of the soluble interaction product corresponds to the species $(n\text{-}BuCdCl)_2$ or $n\text{-}Bu_2Cd\cdot CdCl_2$. Other compounds isolated during the course of these studies were not soluble in cyclohexane.

Redistribution Reactions

Interaction between $(n\text{-}C_4H_9)_2Cd$ and cadmium halides plainly occurs since appreciable solubility of the cadmium halide is effected when the two compounds are allowed to react in ether solvent. Cadmium chloride and iodide are essentially insoluble in diethyl ether alone. Analysis of the supernatant portion from the reaction of $(n\text{-}C_4H_9)_2Cd$ with $CdCl_2$ indicates that the reaction to form RCdX (or $R_2Cd\cdot CdX_2$) in the case of the chloride is not complete, but instead an equilibrium is reached where $K \tilde{=} 5$. Data for the iodide system supports the

conclusion of almost complete reaction in this case. The Cd:I ratios of both the soluble and insoluble portions are very close to 1:1.

The infrared spectra (Figures 5 and 6) confirm the occurrence of an interaction by the appearance of a shoulder at 618 cm^{-1} for n-Bu_2Cd-$CdCl_2$ and at 615 cm^{-1} for n-Bu_2Cd-CdI_2 upon the ν_{as} band arising from the dialkyl cadmium compound in the reaction solution. Also, the absorption of uncomplexed n-Bu_2Cd at 572 cm^{-1} is shifted to slightly lower energies at 565 cm^{-1} and 556 cm^{-1} for the chloride and iodide cases, respectively. In the iodide system, the shoulder at 615 cm^{-1} is nearly as intense as the 644 cm^{-1} absorption, in contrast to the analogous chloride case. The expected disappearance of ν_s for n-Bu_2Cd is not readily apparent because of an interfering solvent band at 500 cm^{-1}.

Infrared spectra of the crystalline products obtained from the soluble portions of the redistribution reactions are shown in Figure 7. The spectra are very similar in appearance below 700 cm^{-1} and there is no evidence for any ether of solvation (gravimetric analysis agrees also). The most plausible assignment of the C-Cd stretching band is near ν_{as} for n-Bu_2Cd, with some displacement due to substitution of one alkyl group by halogen (RCdX) or to distortion of the dialkyl by coordinated CdX_2 ($R_2Cd \cdot CdX_2$). Thus, tentative assignment for the C-Cd stretch is made at 627 cm^{-1} for the iodide product and at the strong double absorption at 636,627 cm^{-1} for the chloride product. It should be pointed out that the very strong band assigned to ν_s in n-Bu_2Cd is not evident in the 1:1:1 solid, as expected.

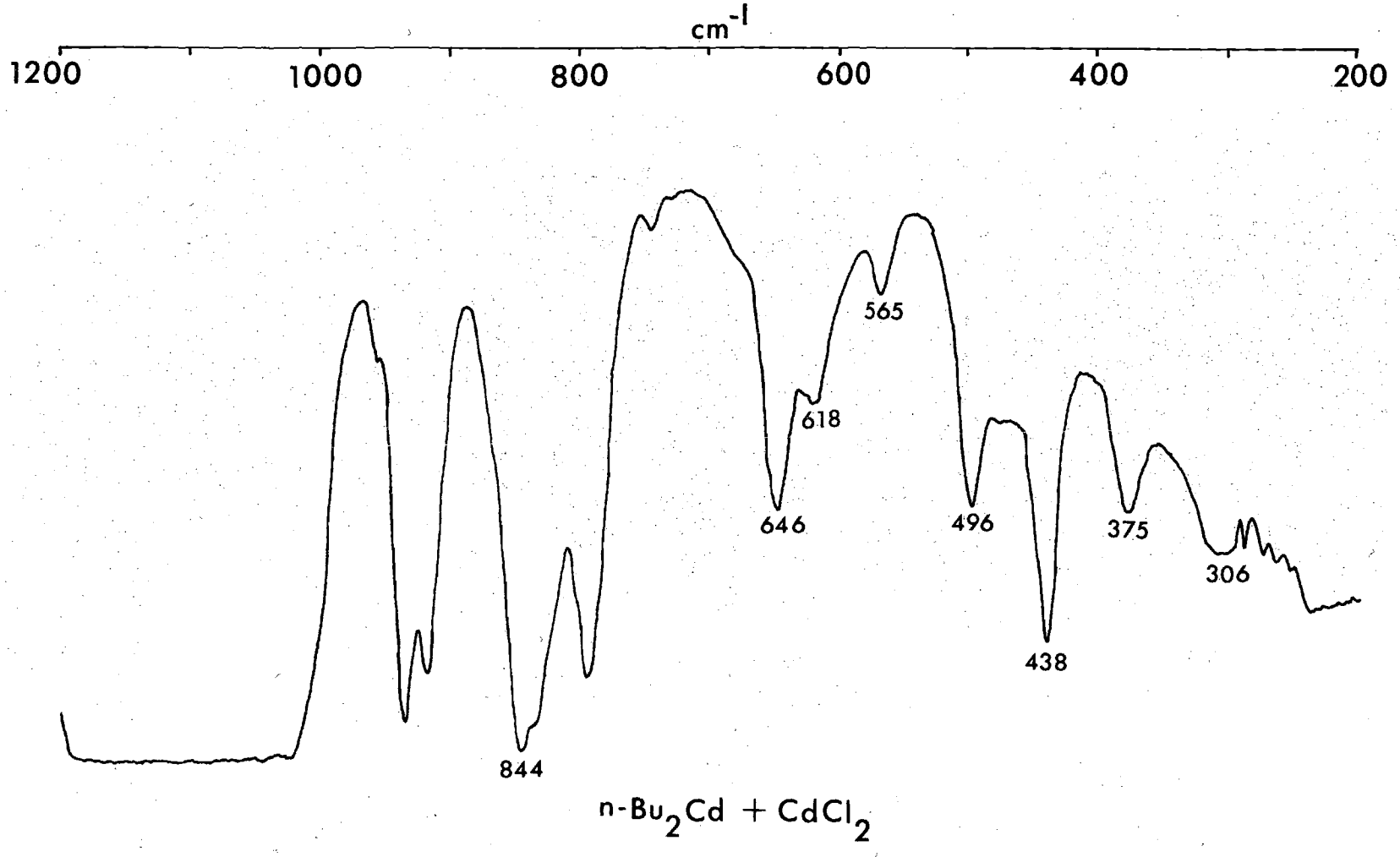


Figure 5. Infrared Spectrum: Supernatant Solution Resulting from an Equimolar Mixture of $(n\text{-}C_4H_9)_2Cd$ and $CdCl_2$ in Diethyl Ether

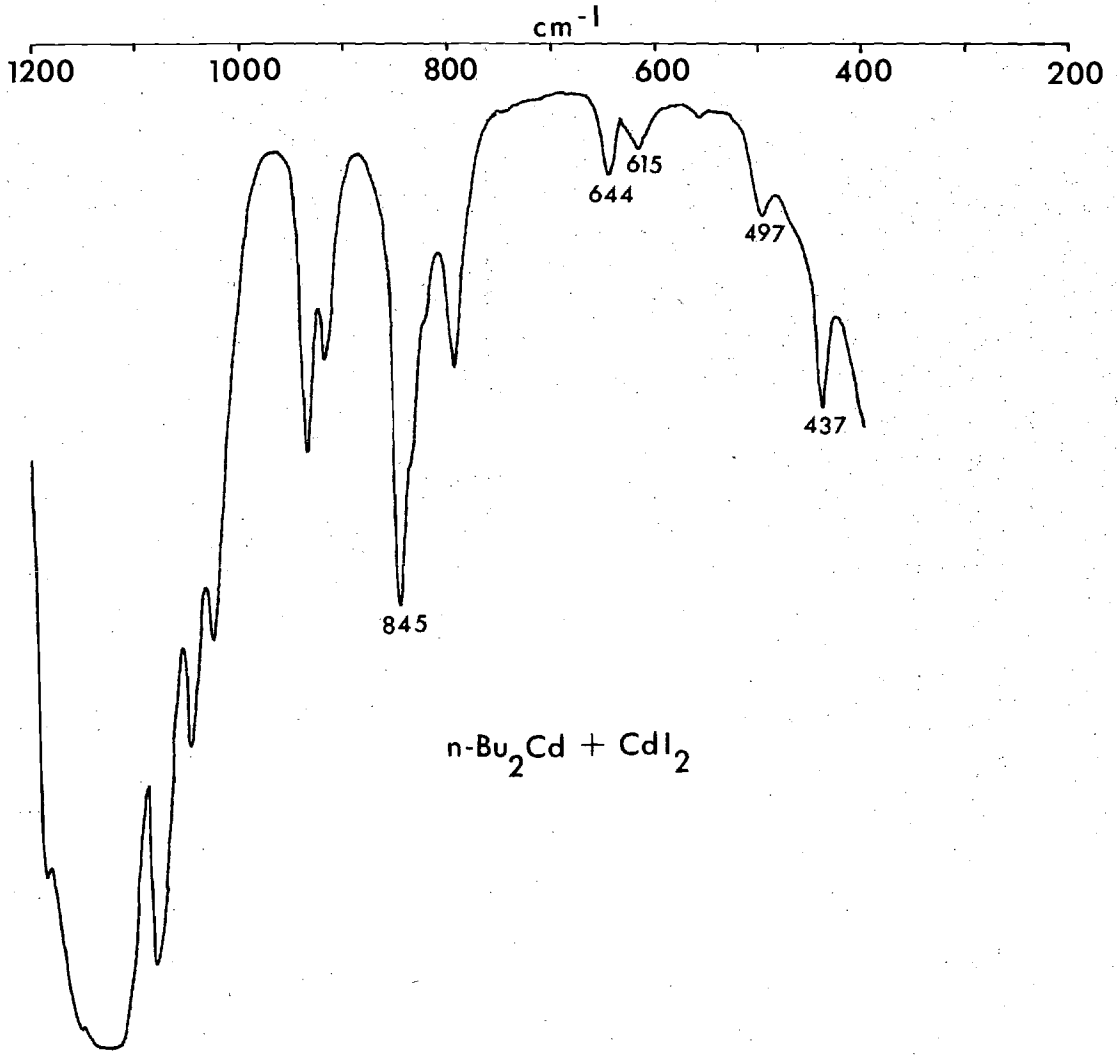


Figure 6. Infrared Spectrum: Supernatant Solution Resulting from an Equimolar Mixture of $(n\text{-}C_4H_9)_2Cd$ and CdI_2 in Diethyl Ether

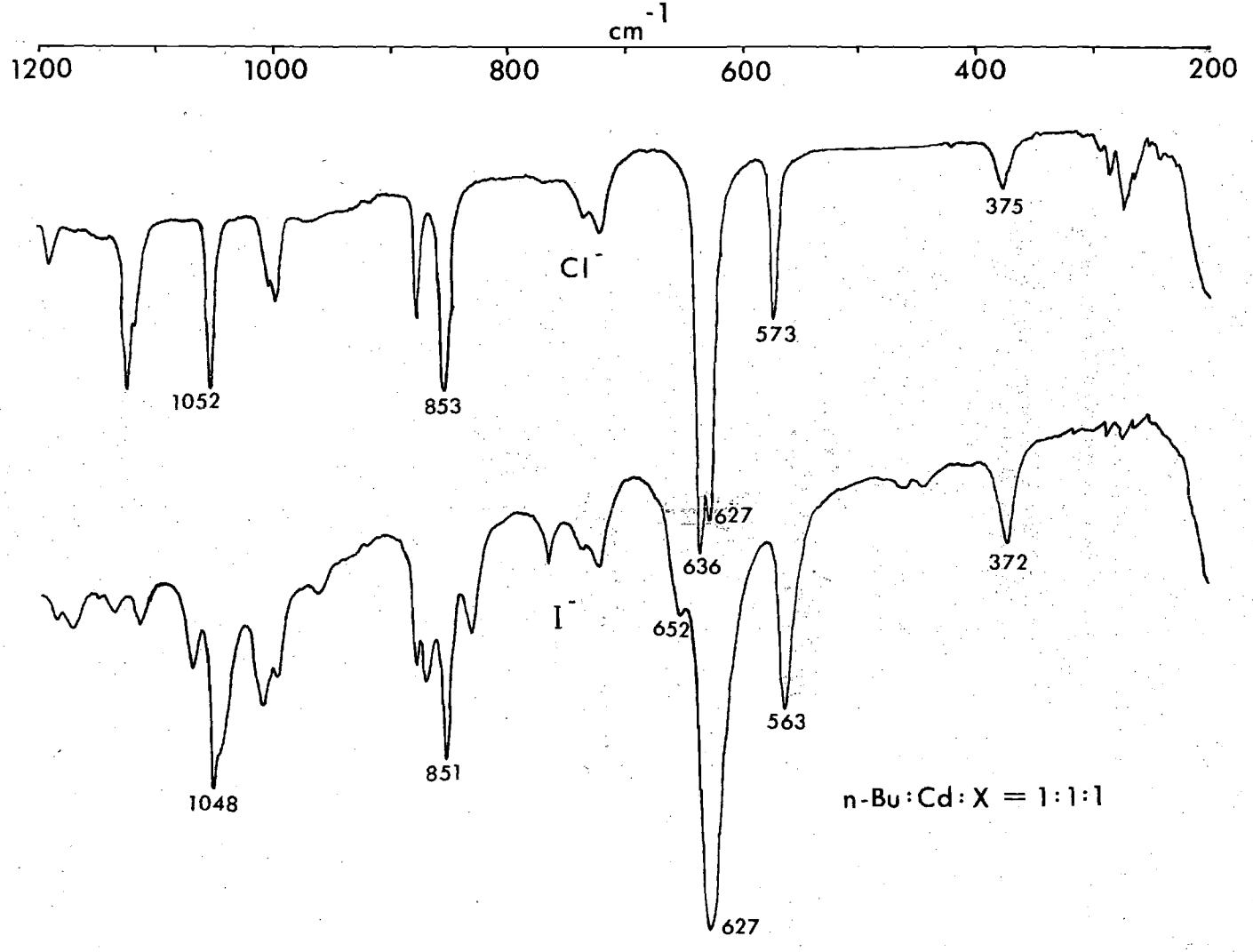


Figure 7. Infrared Spectrum: Products Having the Empirical Formula C_4H_9CdX Isolated from Equimolar Mixtures of $(n\text{-}C_4H_9)_2Cd$ and CdX_2 in Diethyl Ether and Cyclohexane. Upper Curve- X = Cl, Lower Curve- X = I

The spectroscopic and analytical data for mixtures of $(n\text{-}C_4H_9)_2Cd$ and $CdCl_2$ or CdI_2 in cyclohexane are very similar to the observations in diethyl ether. When the halogen is chloride, interaction is not complete and the elemental ratio of the soluble fraction of the reaction mixture was Cd:Cl = 3.7:1.0. In the iodide case, reaction was complete yielding an insoluble product and leaving essentially no dialkyl in solution. Excess cadmium halide was employed in these reactions to assist equilibration of the cadmium dialkyl with the halide.

The corresponding infrared spectra from mixtures in ether and cyclohexane are similar. As in ether, $(C_4H_9)_2Cd$ in cyclohexane shows the same infrared absorption bands as the neat dialkyl with no apparent solvent shifts. The spectrum of the supernatant solution from the mixture containing $CdCl_2$ exhibited a 30 per cent decrease in the intensity of the $(n\text{-}C_4H_9)_2Cd$ infrared bands at 644 cm^{-1}, 570 cm^{-1} and 501 cm^{-1} and the appearance of a shoulder at 653 cm^{-1} and 628 cm^{-1} on the 644 cm^{-1} absorption. The other bands are essentially unchanged. The crystalline solid obtained by cooling the supernatant of this reaction has an infrared spectrum identical to the analogous material isolated from diethyl ether (Figure 7).

For the reaction of $(n\text{-}C_4H_9)_2Cd$ with CdI_2 in cyclohexane, the infrared bands attributable to dialkyl cadmium disappear almost completely and no others appear. The insoluble product of this reaction has an infrared spectrum identical to the compound isolated from ether, having the ratio of components: C_4H_9:Cd:I = 1:1:1 (Figure 7).

From comparison of the data for the ether and cyclohexane solvent systems, it is apparent that solvent basicity plays little part in the interaction process between $(n\text{-}C_4H_9)_2Cd$ and $CdCl_2$ or CdI_2. It was anticipated that the use of a non-donor solvent, such as cyclohexane, might permit the integrity of the soluble interaction compound of empirical formula, $n\text{-}C_4H_9CdCl$, previously isolated only by cooling the solution portion of the redistribution mixtures in diethyl ether. Since essentially identical results are obtained in both solvents, a process not related to solvent basicity is indicated.

Thus, a definite interaction between $(n\text{-}C_4H_9)_2Cd$ and CdX_2 does occur in ether solution and a compound of the empirical formula C_4H_9CdX can be isolated. However, without molecular association data it cannot be concluded that alkyl exchange has occurred. The following discussion of infrared studies of the products of the reaction between Grignard reagents and cadmium halides will disclose additional pertinent arguments for the existence of RCdX species.

The Organocadmium Reagent

On the basis of the Gilman test, the Grignard reagent reacts quickly and quantitatively with cadmium halides in diethyl ether. The products are unstable at room temperature in the presence of light and cannot be stored for long periods except when kept cold in the dark.

The Reactions of Grignard Compounds with Cadmium Halides

A. $RMgX:CdX_2 = 2:1$

The (2:1) mixture is the common *in situ* reagent which is used in organic synthesis (X usually Cl). Happily, this stoichiometry is also the most straightforward in explanation. Analysis, the Gilman

test, and the infrared spectra indicate that the products are n-Bu_2Cd and MgX_2 alone. Where X = I, the halide has high solubility and no solid residue is present; but when X = Cl, the halide is insoluble and is isolated as very pure $MgCl_2 \cdot Et_2O$ (Spectrum: Figure 11, 2:1). $MgI_2 \cdot nEt_2O$ may be isolated by cooling the (2:1) solution and compares well, in the infrared, with the $MgI_2 \cdot nEt_2O$ shown in Figure 14.

Interaction between n-Bu_2Cd and magnesium halide is evident for X = Cl, I. For the Cl^- case, it is seen by analysis that $MgCl_2$ is soluble in ethereal n-Bu_2Cd to give a solution ca. 0.02 M in $MgCl_2$, whereas the halide is normally insoluble in diethyl ether. The Cd:Mg ratio of this solution, 3.7:1.0, did not imply strong interaction. The infrared spectrum shows evidence of coordination of $MgCl_2$ by n-Bu_2Cd (Figure 10) and is similar to the spectrum of the dialkyl alone in ether solution. A slight alteration is an indistinct shoulder at 618 cm^{-1}, in the same position as the shoulder previously attributed to RCdX or $R_2Cd \cdot CdX_2$. The absorption ν_{as} of n-Bu_2Cd itself has a poorly defined shoulder on the low energy side.

When X = I, a solution is obtained containing the dialkyl cadmium compound and magnesium halide in the molar ratio 1:2, respectively. Removal of solvent produces no solid $MgX_2 \cdot nEt_2O$, indicating solubility of the etherate in n-Bu_2Cd; alternatively, this could be a mixture of n-Bu_2Cd and molten MgI_2 etherate, with no interaction. The infrared spectrum (Figure 13) of this solution exhibits several bands characteristic of MgI_2 in ether (308,460,504,773,833,894 cm^{-1}) plus the familiar pattern of di-n-butyl cadmium. The band assigned to ν_{as} (C-Cd) is shifted slightly to 641 cm^{-1}, and again, a shoulder at 614 cm^{-1} is

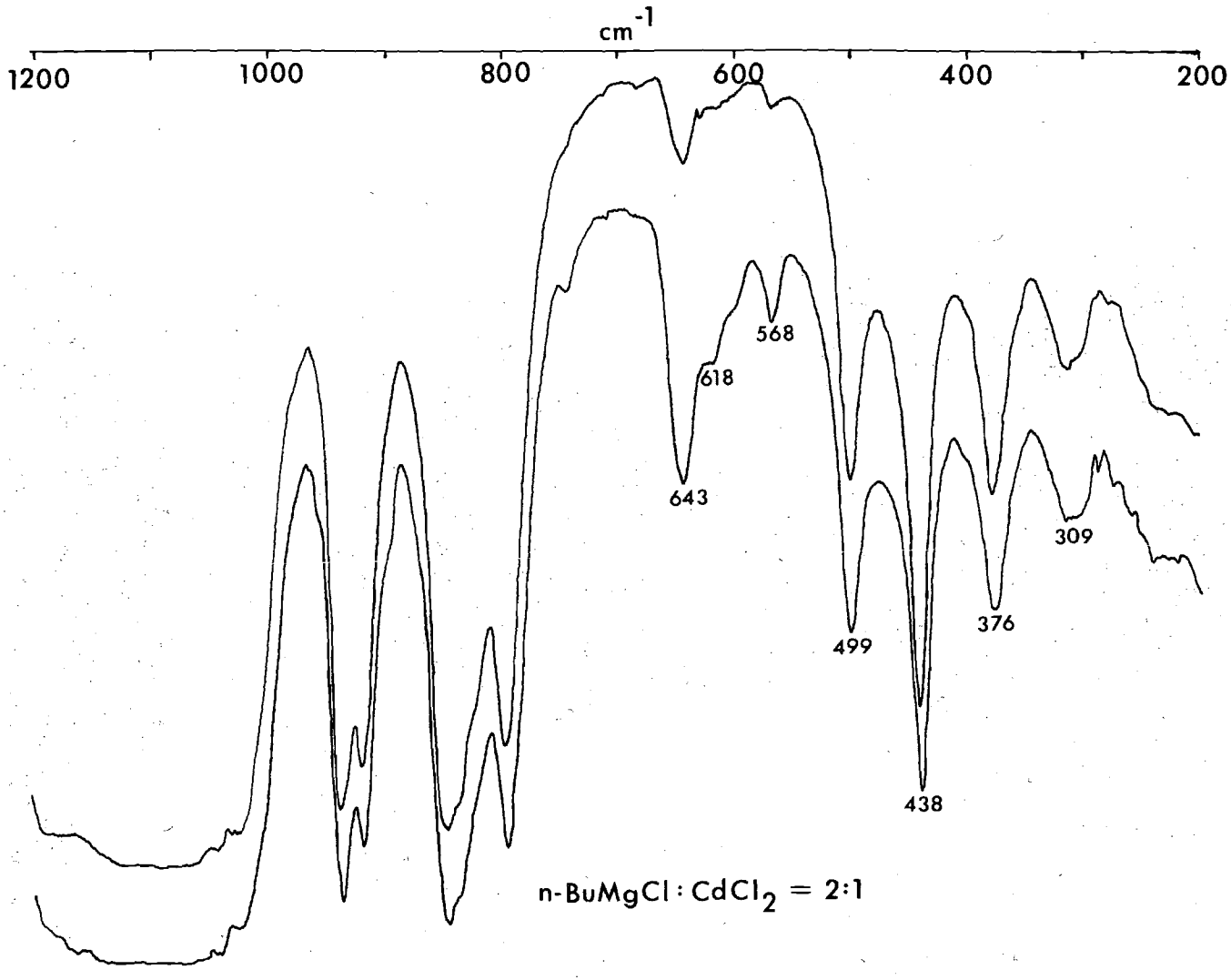


Figure 10. Infrared Spectrum: Supernatant Solution from the Reaction of $n\text{-}C_4H_9MgCl$ with $CdCl_2$ in Diethyl Ether in 2:1 Ratio. Upper Curve- Dilute Solution, Lower Curve- Concentrated Solution

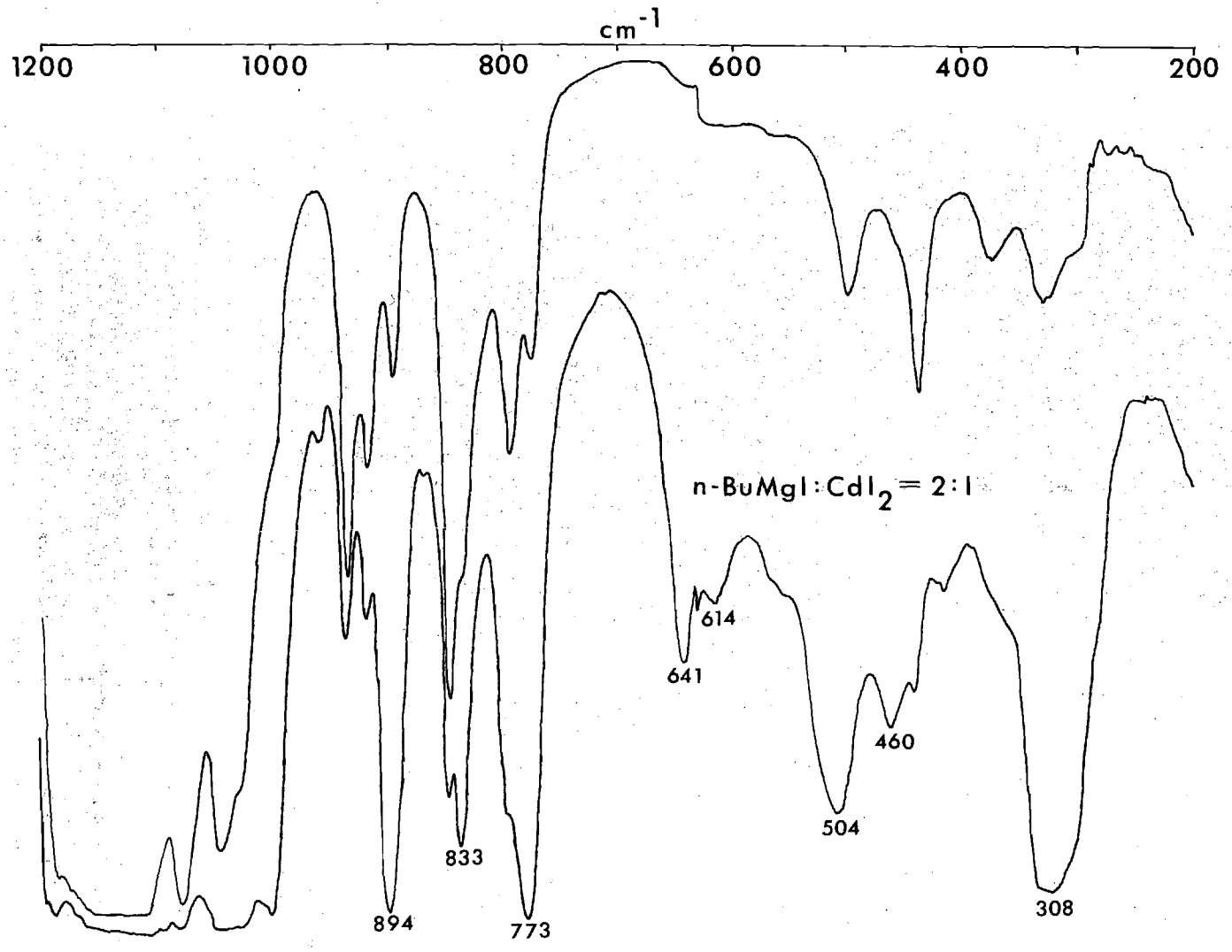


Figure 13. Infrared Spectrum: Supernatant Solution from the Reaction of $n\text{-}C_4H_9MgI$ with CdI_2 in Diethyl Ether in 2:1 Ratio. Upper Curve- Dilute Solution, Lower Curve- Concentrated Solution

suggestive of that observed for the I^- resistribution reaction (615 cm^{-1}).

The shoulder observed for both n-Bu_2Cd-CdX_2 and n-Bu_2Cd-MgX_2 mixtures suggests that the interaction is of the type $R_2Cd \cdot MX_2$, where the halide is coordinated by halogen bridges. The assignment of the shoulder absorption would thus become a vibration associated with the distorted n-Bu_2Cd and would reasonably be found at lower energy.

The Reaction of Grignard Compounds with Cadmium Halides

B. $RMgX:CdX_2 = 1:1$

Assuming stepwise alkylation of CdX_2 by the Grignard reagent, the 1:1 reaction mixture would yield initially equimolar quantities of RCdX and MgX_2. However, it has been demonstrated already that disproportionation processes, as represented in equation (10), are important under the conditions of the experiment. Thus, the description of this mixture requires a combination of arguments from other systems described earlier.

Where X = Cl, $MgCl_2$ is solubilized to some extent by the cadmium species which are present. Also, the solubility of $MgCl_2$ in this product mixture is higher than the solubility of $MgCl_2$ in ether solutions of dibutyl cadmium (0.05M vs. 0.02M). The Cd:Cl ratio of the soluble fraction is approximately the same as that found for mixtures of $(n\text{-}C_4H_9)_2Cd$ and $CdCl_2$ in diethyl ether, indicating that the disproportionation equilibria (equation 10) are unchanged by the interaction with $MgCl_2$.

Infrared spectra of the soluble portion of the 1:1 mixture where X = Cl (Figure 9) show only minor differences from the spectrum of the 2:1 reaction (Figure 10). The pattern of absorption due to $(n\text{-}C_4H_9)_2Cd$-

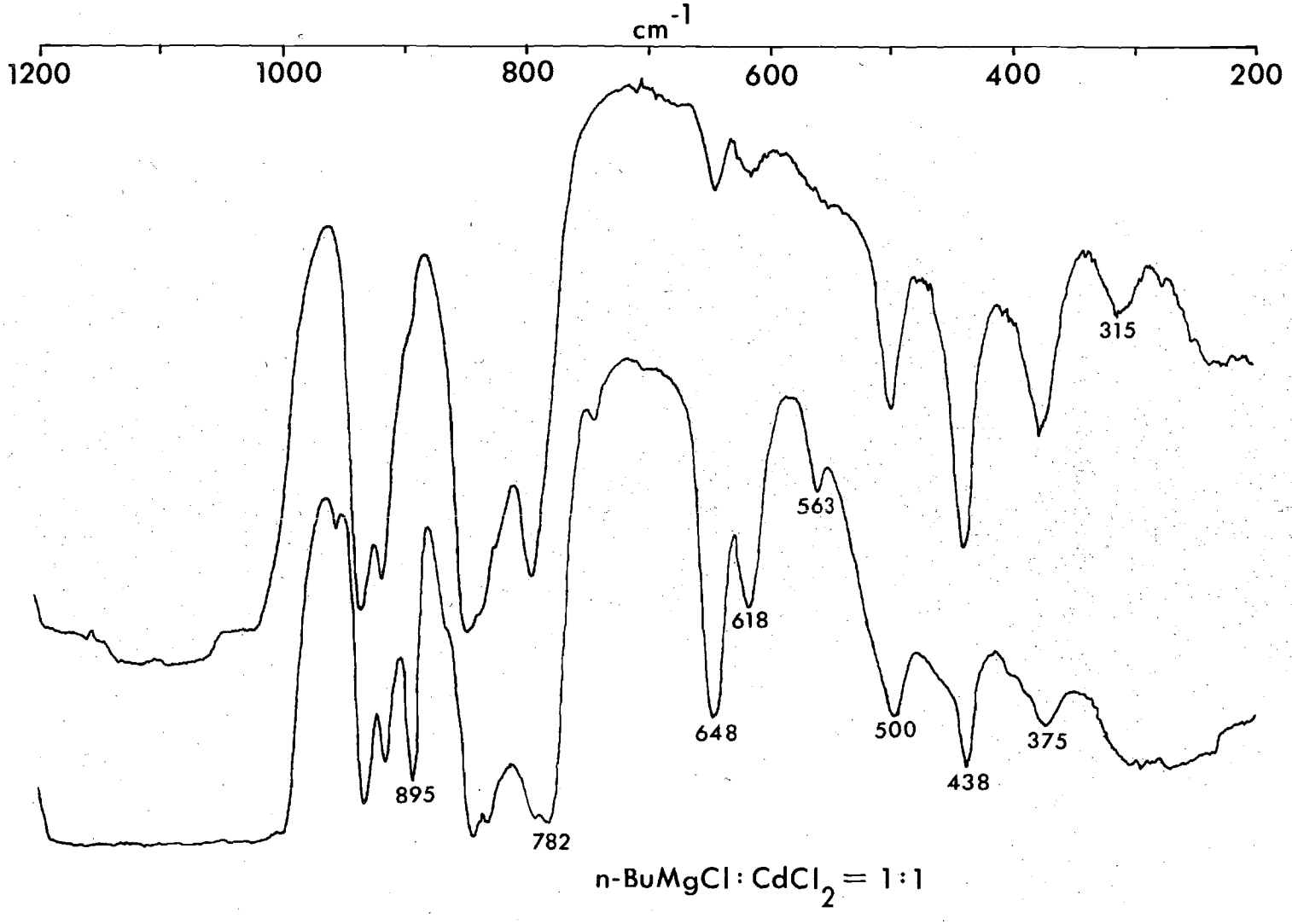


Figure 9. Infrared Spectrum: Supernatant Solution from the Reaction of $n\text{-}C_4H_9MgCl$ with $CdCl_2$ in Diethyl Ether in 1:1 Ratio. Upper Curve- Dilute Solution, Lower Curve- Concentrated Solution

$CdCl_2$ mixtures is evident, along with two new bands at 895 cm^{-1} and 782 cm^{-1} which may plausibly be ascribed to the presence of $MgCl_2$.

For the mixtures where X = I, the results are similar to the case above except that the by-product halide, MgI_2, is soluble. The presence of a large amount of soluble magnesium halide causes an apparent shift in the $(n\text{-}C_4H_9)_2Cd\text{-}CdI_2$ interaction equilibrium from Cd:I = 1.1:1.0 in the absence of MgI_2, to Cd:I = 2.3:1.0 when MgI_2 is present. The infrared spectra (Figure 12) of the soluble portion of the reaction mixture exhibit absorption bands arising from $(n\text{-}C_4H_9)_2Cd\text{-}CdI_2$ interaction with additional bands at 325, 775, and 895 cm^{-1}. These three latter absorption bands are found also in ethereal solutions of MgI_2 alone and cannot be said to be the result of interaction with cadmium species. They are more plausibly described as halide-solvent interactions.

Spectra of the insoluble material from the 1:1 reactions indicate that $MgCl_2 \cdot Et_2O$ (Figure 11) and $MgI_2 \cdot nEt_2O$ (Figure 14) are the predominant absorbing species in these residues. Elemental analysis supports the conclusion that the solid residues are, for the most part, mixtures of magnesium and cadmium halides. Little absorption is noted in the region 600-650 cm^{-1} where R-Cd vibrations are expected.

To summarize, the 1:1 reaction proceeds as expected, to yield magnesium halide and an equilibrium mixture of $(n\text{-}C_4H_9)_2Cd$ and CdX_2. From the increased solubility of $MgCl_2$, it may be said that interaction with the soluble cadmium species is responsible. The infrared spectra support the conclusion that both CdX_2 and MgX_2 are coordinated by $(n\text{-}C_4H_9)_2Cd$ in the same manner. A good model for this interaction

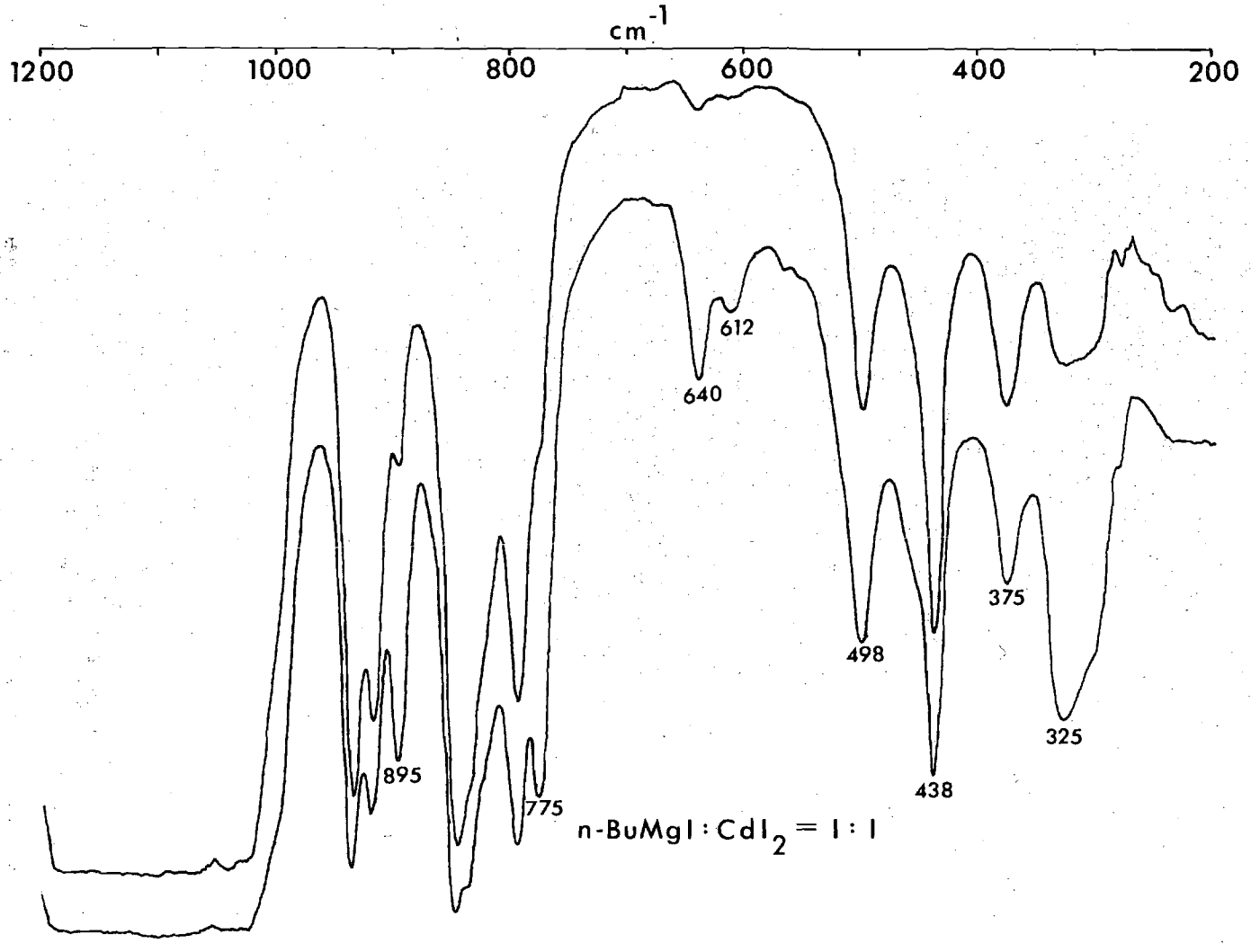
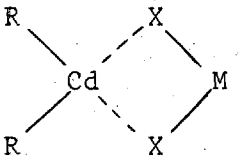
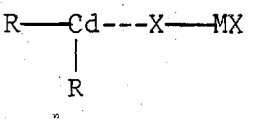


Figure 12. Infrared Spectrum: Supernatant Solution from the Reaction of n-C_4H_9MgI with CdI_2 in Diethyl Ether in 1:1 Ratio. Upper Curve- Dilute Solution, Lower Curve- Concentrated Solution

might be a structure such as II, where cadmium may assume a coordination number of four. Alternatively, a singly-bridged species, III, is



(II)



(III)

possible. Although coordination of the halides to dialkyl cadmium species is pictured above, it is possible that a finite concentration of RCdX species is present, and that this also may coordinate additional cadmium or magnesium halide. The infrared solution spectra do not distinguish this latter possibility from the predominant interactions with dialkyl cadmium.

In comparison, the 2:1 reaction produces only R_2Cd and MgX_2, and interaction between these two compounds was demonstrated in the infrared spectra and from enhanced solubility of magnesium halides.

Evidence for RCdX

It has been demonstrated above that R_2Cd-CdX_2 interactions and R_2Cd-MgX_2 interactions are similar in terms of the infrared spectrum of the soluble species, suggesting the interaction forms II and III which do not involve an alkyl-halogen exchange. Also, analytical data show that the interaction is incomplete at room temperature.

If, however, the soluble fractions of R_2Cd-CdX_2 or 1:1 RMgX-CdX_2 mixtures are cooled in dry ice, white solids are precipitated which

have strikingly similar infrared spectra. The $(n\text{-}C_4H_9)_2Cd\text{-}CdX_2$ (X = Cl,I) soluble fractions yield flaky crystalline solids with the empirical formula C_4H_9CdX, and having the infrared spectra shown in Figure 7. The soluble fractions of the 1:1 $RMgX\text{-}CdX_2$ (X = Cl, I) mixtures yield white solids which have the elemental ratios Mg:Cd:X = 1:1:3 and whose infrared spectra are shown in Figure 8.

For each set of spectra it is noted that there are only minor changes in the absorption pattern when Cl is substituted for I. The only exception to this similarity is for the Mg:Cd:Cl = 1:1:3 species below 400 cm^{-1}. Of particular interest are the bands at 627 and 563 cm^{-1} for the 1:1:1 and 1:1:3 iodide species, and at 636, 627 and 573 cm^{-1} for the chloride species. These absorptions are in the region where the C-Cd stretch is expected, the bands at 627, 636 cm^{-1} having the greatest intensity and being the logical choices for a C-Cd stretching vibration. The absorptions at 573 and 563 cm^{-1} are always present for the n-butyl alkyl-cadmium species and show minor shifts of a few cm^{-1} for different situations; however, they have been excluded as C-Cd stretching absorptions because of their relatively lower intensities compared to the absorptions at ca. 630 cm^{-1}.

The infrared spectra for these two products indicate that they probably have the same alkyl-cadmium arrangement since the band attributed to the C-Cd stretching vibration is unchanged for both materials. The empirical formula RCdX may be representative of three situations here: (a) monomer RCdX (i=1.0), (b) polymer $(RCdX)_n$ (i=n), and (c) unsymmetrical dimer $R_2Cd\cdot CdX_2$ (i=2). The isolation of a solid with elemental ratios Mg:Cd:X = 1:1:3 in addition to having characteristic

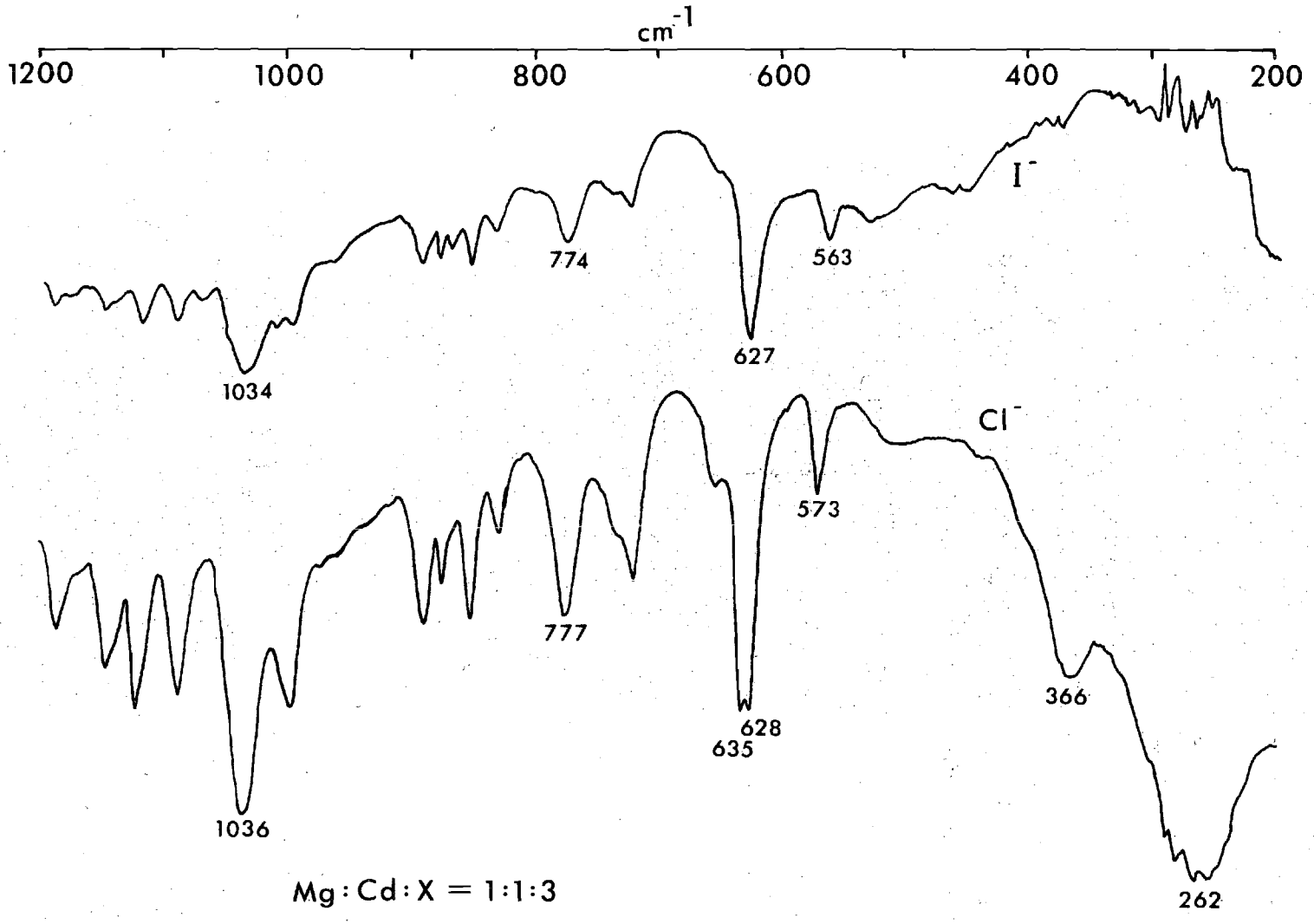
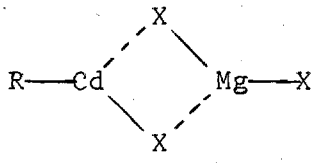


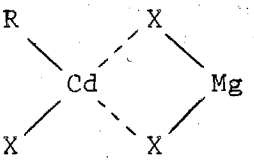
Figure 8. Infrared Spectrum: Solids Isolated from the Soluble Portion of the Reaction Mixture of n-C_4H_9MgX with CdX_2 in Diethyl Ether. Elemental Ratios are Mg:Cd:X = 1:1:3. Upper Curve- X = I, Lower Curve- X = Cl

infrared bands at 627 and 636 cm^{-1} suggests that this material is the product $RCdX \cdot MgX_2$. This would seem to rule out $R_2Cd \cdot CdX_2$ as a likely form since the required empirical formula would then be $R_2Cd \cdot CdX_2 \cdot 2MgX_2$, a species without substantial precedent.

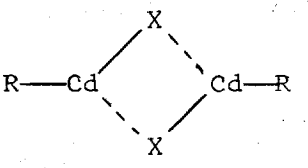
A preferred configuration for the 1:1:3 solid is thought to be that of structures IV or V, and for the RCdX species structure VI is proposed. The 1:1:3 solid isolated in these systems is analogous to



IV



V



VI

the RMg_2X_3 species isolated from tetrahydrofuran solutions of C_2H_5MgCl (37).

The structures represented above may be oversimplifications of the solid state arrangements; however, these forms do demonstrate the expected types of aggregation anticipated for these compounds. For example, the solid state structures of $C_2H_5MgBr \cdot 2(C_2H_5)_2O$ (38) and $C_6H_5MgBr \cdot 2(C_2H_5)_2O$ (39) consist of discrete monomers in the solid state, association being prevented by the steric requirement of the solvating ether molecules. On the other hand, unsolvated ethyl zinc iodide consists of polymeric chains with Zn-I bridges in the solid state.

In summary, it is concluded that the evidence presented is only indicative and does not conclusively demonstrate the existence of an RCdX species in solution or in the solid state.

CHAPTER IV

CONCLUSIONS

An interaction was demonstrated between $(n\text{-}C_4H_9)_2Cd$ and cadmium halides in diethyl ether and cyclohexane. This interaction was observed to be more complete with cadmium iodide than with cadmium chloride. A compound of empirical formula C_4H_9CdX was isolated, but lack of molecular association data prohibited discrimination between RCdX monomer or polymer species and $R_2Cd \cdot CdX_2$ species.

Grignard reagents were found to react with cadmium halides, in 2:1 ratio, to produce the corresponding dialkyl cadmium compound and magnesium halide. Evidence was presented for $R_2Cd\text{-}MgX_2$ interaction through infrared data and solubility effects.

In 1:1 ratio, Grignard reagents and cadmium halides react to produce magnesium halide and a mixture of CdX_2 and R_2Cd which interact as described above. Magnesium halides were observed to compete with cadmium halides in interactions with the dialkyl cadmium compound, and spectroscopically these interactions appeared to be of a similar type. A compound having the elemental ratios of Mg:Cd:X = 1:1:3 was isolated.

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PART III

A STUDY OF THE REACTIONS OF LITHIUM ALUMINUM HYDRIDE AND SODIUM ALUMINUM HYDRIDE WITH BERYLLIUM CHLORIDE IN DIETHYL ETHER AND TETRAHYDROFURAN

CHAPTER I

INTRODUCTION

There is very little published literature which defines the products of the reaction of complex metal hydrides of aluminum such as $LiAlH_4$ or $NaAlH_4$ with beryllium halides in ether solvents. In 1951 Wiberg and Bauer (1) reported that the reaction of $LiAlH_4$ with $BeCl_2$ in diethyl ether proceeds as shown in equation (1) to yield beryllium aluminum hydride $Be(AlH_4)_2$ and LiCl. The insoluble LiCl was reported to precipitate from solution leaving dissolved $Be(AlH_4)_2$ which was recovered by removal of solvent.

$$2LiAlH_4 + BeCl_2 \rightarrow Be(AlH_4)_2 + 2LiCl \qquad (1)$$

Wood and Brenner (2) reported that metastable solutions of $Be(AlH_4)_2$ could be prepared by combining $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether. It was reported that a white precipitate formed and was filtered from the solution leaving a filtrate having the elemental analysis, Be/Al/H = 1.0/1.82/9.2, indicating the presence of $Be(AlH_4)_2$ in solution. The product was said to decompose within a few hours at the boiling point of ether; however, it was stable for several days at temperatures below 10°C. The solution could be stabilized by the addition of $BeCl_2$ or $AlCl_3$. The absence of data other than analysis leaves this product poorly described. The decomposition products were not characterized.

In other work (3), the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether has been shown to yield a precipitate of LiCl and BeH_2, leaving AlH_3 in solution.

Related to the work above is the reported preparation of $LiBe(AlH_4)_3$ which has been described in a recent patent (4). This compound was prepared by the addition of $LiAlH_4$ in diethyl ether to a slurry of $BeCl_2$ in a mixture of ether and hexane, at room temperature, in 2:1 ratio. Immediate precipitation resulted and the precipitated solid was removed as soon as the combination of reagents was completed. After addition of triethylamine to the filtrate, a solid having the empirical formula $LiBe(AlH_4)_3$ precipitated over a period of seven days. The yield was ca. 5 per cent based on $BeCl_2$. The compound was characterized by elemental analysis and characteristic X-ray powder diffraction pattern. An explanation of the results claimed in this work may be formulated (equation 2) based on the results reported in prior art. If $Be(AlH_4)_2$ were formed initially and reacted preferentially with the

$$4LiAlH_4 + 2BeCl_2 \rightarrow [Be(AlH_4)_2 + BeCl_2 + 2LiAlH_4 + 2LiCl] \qquad (2)$$

$$\rightarrow LiBe(AlH_4)_3 + \tfrac{1}{2}BeH_2\downarrow + AlH_3 + \tfrac{1}{2}BeCl_2 + 3LiCl\downarrow$$

$LiAlH_4$ reactant to form a stable adduct, the complex might be isolated after removal of the insoluble products. The addition of triethylamine to the product solution may serve to prevent disproportionation of the complex, or to induce precipitation of the complex.

As can be seen from the literature cited above, there are conflicting descriptions of the reaction of $LiAlH_4$ and $BeCl_2$ in ether solvents. From analogous studies (5) of reactions of $LiAlH_4$ and $NaAlH_4$ with MgX_2 (X = Cl,Br,I) in diethyl ether and tetrahydrofuran, it was found that halogen atoms were replaced in a stepwise fashion in a simple metathetical exchange process to yield $XMgAlH_4$ and/or $Mg(AlH_4)_2$. The nature of the products was controlled by the choice of halogen and the solvent type. Reaction of zinc (6), cadmium (7), and mercury (7) halides with $LiAlH_4$ in diethyl ether or tetrahydrofuran produced only the insoluble, unstable binary hydrides ZnH_2, CdH_2, HgH_2 which decomposed to the metal and hydrogen gas at or below room temperature. Aluminum hydride was left in solution and it was postulated that $M(AlH_4)_2$ was formed as an intermediate, which then rapidly decomposed according to equation (3). The reaction of $NaAlH_4$ and $CaCl_2$ in 2:1 ratio is reported to yield $Ca(AlH_4)_2$ and NaCl (22).

$$M(AlH_4)_2 \rightarrow MH_2 + AlH_3 \quad (M = Zn,Cd) \tag{3}$$

Recent Russian work (23) has reported the preparation of $LiAl_2H_7$ and $LiAl_3H_{10}$ in diethyl ether according to the stoichiometries shown in equations (4a) and (4b). The compounds $LiAl_2H_7$ and $LiAl_3H_{10}$ were

$$2\ LiAlH_4 + BeCl_2 \rightarrow LiAl_2H_7 + HBeCl + LiCl \tag{4a}$$

$$3\ LiAlH_4 + BeCl_2 \rightarrow LiAl_3H_{10} + BeH_2 + 2LiCl \tag{4b}$$

reported to be very unstable in ether but somewhat more stable in the solid state as crystals.

Purpose

Since the published data are in disagreement concerning the course of the reaction when $LiAlH_4$ and $BeCl_2$ are combined in diethyl ether, this reaction was reexamined in an attempt to clarify the conflicting reports. The reaction of $LiAlH_4$ and $NaAlH_4$ with $BeCl_2$ in tetrahydrofuran solvent was also studied. Using elemental analysis, infrared spectroscopy and X-ray powder diffraction techniques the above systems were studied in an attempt to characterize the reaction products.

CHAPTER II

EXPERIMENTAL AND INSTRUMENTATION

Reagents

Beryllium metal was obtained from the Brush Beryllium Company, Elmore, Ohio. The metal was in the form of high purity electrorefined flake. Purity assay is given in Part I.

Chlorine gas was Matheson high purity, used without further purification.

All solvents were distilled at atmospheric pressure from $LiAlH_4$ (diethyl ether) or $NaAlH_4$ (benzene, tetrahydrofuran) immediately before use.

$LiAlH_4$ and $NaAlH_4$ were obtained as gray, lumpy solids from Ventron, Metal Hydrides Division.

Analytical

Aluminum was determined by a back-titration method at pH 4 using dithizone (diphenylthiocarbazone) as the indicator. To the sample was added 10 per cent excess standard EDTA solution, followed by adjustment of pH using dilute (1:1) ammonium hydroxide until the solution was just alkaline to methyl red. The solution was then boiled for two minutes, cooled to room temperature or below, and approximately 10 ml of pH 4 buffer was added. Ethanol was then added to give ca. 40-50 per cent, by volume, ethanol. After dithizone indicator was added, the sample was titrated with standard zinc acetate solution to an equivalence

point signified by a color change from blue-green to pink. Beryllium in equimolar amounts does not interfere.

Beryllium was determined gravimetrically by precipitation as the hydroxide, followed by ignition to the oxide at 1000°C for one hour (8). Aluminum interference was prevented by the addition of an excess of EDTA which complexes the aluminum and prevents its precipitation as the hydroxide.

Analysis for chloride was done using the modified Volhard procedure. Chloride was precipitated as AgCl by the addition of excess standard $AgNO_3$. Benzyl alcohol was added to coat the halide precipitate and the solution was back-titrated with standard KCNS using ferric ion as the indicator.

Hydrogen analysis was accomplished by acid hydrolysis of a weighed amount of sample and collecting the evolved gas in a calibrated gas buret. Hydrolysis was carried out in an organic diluent (diglyme or benzene) to moderate the reaction. A dry ice trap prevented any condensable vapor from entering the measuring volume

Preparative Methods

All operations were carried out under an atmosphere of dry, oxygen-free nitrogen in the dry box or using bench-top inert atmosphere techniques (9).

Standard Solutions of Complex Aluminum Hydrides

Solutions of $LiAlH_4$ in diethyl ether and tetrahydrofuran and solutions of $NaAlH_4$ in tetrahydrofuran were prepared by stirring the solid hydride for 24 hours with the appropriate solvent, followed by

filtration, to yield a clear, colorless solution. These reactant solutions were standardized by aluminum analysis and transferred volumetrically.

Beryllium Chloride Solvates

Beryllium chloride was prepared using a hot tube reaction described in Part I. Argon was used as a carrier gas instead of nitrogen, resulting in an almost quantitative yield of $BeCl_2$. To prepare the etherates of $BeCl_2$, a quantity of the unsolvated halide was suspended in dry benzene and the mixture cooled in an ice-water bath. A quantity (50 per cent excess based on the bis-solvate) of dry diethyl ether or tetrahydrofuran was added slowly as the mixture was stirred. The solvated, crystalline $BeCl_2$ was recovered by filtration and dried at reduced pressure. Analysis for $BeCl_2 \cdot 2THF$ gave the following results: Be- found 3.93%, calc. 4.02%; Cl- found 30.9%, calc. 31.6%. For $BeCl_2 \cdot 2Et_2O$ the results were: Be- found 3.86%, calc. 3.95%; Cl- found 30.5%, calc. 31.1%. Infrared and X-ray powder diffraction data were recorded.

$LiAlH_4$ + $BeCl_2$ in 2:1 Ratio in Diethyl Ether

To 32.29 mmoles of $BeCl_2$ in 250 ml of diethyl ether was added 64.58 mmoles of $LiAlH_4$ solution. The solution was cooled in an ice-water bath as the hydride addition was made. A white precipitate formed at once and increased in volume as more $LiAlH_4$ was added. The mixture was stirred for 15 hours and filtered through a glass frit, yielding a white residue and a colorless, clear filtrate. Removal of solvent from the filtrate yielded a white powder.

Analysis of the insoluble residue indicated the following: H- 2.64%, Be-7.72%, Al-6.43%, Cl-60.6%. The X-ray powder diffraction pattern contained only lines arising from LiCl. The infrared spectrum (nujol mull) exhibited very broad absorptions at 1755, ca. 1350, and 768 cm^{-1}.

Analysis of the ether-soluble fraction gave the following results: H-5.99%, Li-0.73%, Al-50.2%; no beryllium or chloride was recovered in this material. The powder diffraction pattern contained no lines attributable to LiCl or starting materials. The infrared spectrum of a nujol mull of this material showed the following absorptions: 1755 (s,v.br.), 1660 (s,v.br.), 1022 (s), 720 (s,br.), 605 (m).

A similar experiment was performed at -78°C, stirred at this temperature for 60 minutes and filtered in the cold. Again, a white residue was recovered, leaving a clear, colorless filtrate. Analysis of the insoluble residue gave the following results: H-2.40%, Be-7.50%, Al-8.55%, Cl-60.6%. The infrared spectrum of a nujol mull of the insoluble residue gave the following absorptions: 1750 (s,v.br.), 1350 (s,v.br.), 765 (m,v.br.), 316 (s,br.). The X-ray powder diffraction pattern indicated no lines other than those arising from LiCl. The solid isolated by removing solvent from the ether-soluble fraction of this reaction gave the analysis: H-5.98%, Li-0.78%, Al-50.2%, again, no beryllium or halogen was found. The infrared spectrum had absorptions at: 1778 (s,v.br.), 1600 (s,v.br.), 1020 (s,br.), 720 (s,br.), 597 (s, br.). The X-ray powder diffraction pattern showed no lines attributable to LiCl or starting materials. Recovery of elements from these reactions averaged 85 to 90 per cent.

Equilibration of a 2:1 mixture of $LiAlH_4$ and $BeCl_2$ in diethyl ether for 135 hours at 25°C yielded products with infrared spectra identical to the products isolated when the reaction mixture was worked up immediately. The X-ray powder pattern of the insoluble product exhibited only lines of LiCl.

$NaAlH_4$ + $BeCl_2$ in 2:1 Ratio in Tetrahydrofuran

To a stirred suspension of 20.87 mmoles of $BeCl_2 \cdot 2THF$ in 150 ml of tetrahydrofuran, cooled to 0°C in an ice-water bath, was added 41.74 mmoles of $NaAlH_4$ solution. An immediate precipitation resulted. After stirring for 30 minutes at 0°C, the mixture was filtered in the cold yielding a white residue and clear, colorless filtrate. Removal of tetrahydrofuran from this filtrate at reduced pressure produced a white solid.

Analysis of the insoluble fraction of this reaction indicated the following composition: H-1.36%, Be-5.61%, Al-1.91%, Cl-46.9%. The X-ray powder diffraction pattern of this sample contains five unidentified lines in addition to those arising from NaCl. The infrared spectrum of a nujol mull of this sample exhibited the following absorptions: 1710 (s,v.br.), 1350 (s,v.br.), 1020 (w), 815 (s,v.br.).

Analysis of the residue from the soluble fraction of this reaction shows the composition: H-3.05%, Be-0.309%, Al-26.2%, Cl-0.763%. The X-ray powder diffraction pattern of this sample had many lines, but none due to $BeCl_2 \cdot 2THF$. The infrared spectrum of a nujol mull shows absorptions at the following positions: 1800 (s,br.), 1625 (m,v.br.), 1015 (s,br.).

This reaction was repeated and the products stirred together at

room temperature for a period of time to allow possible product redistribution. To 10.39 mmoles of $BeCl_2 \cdot 2THF$ in 75 ml of tetrahydrofuran was added 20.77 mmoles of $NaAlH_4$. The reaction was initiated at room temperature, producing an immediate white precipitate, and the mixture was stirred for 92 hours. At the end of the equilibration period, no obvious further solubilization had occurred and the mixture consisted of a fine white solid suspension. Filtration of this mixture produced a white residue and a colorless filtrate. Infrared examination of the filtrate showed the following absorptions (THF bands deleted): 1640 (s), 793 (s), 726 (s). Nmr spectra of the filtrate indicated nothing other than solvent over a 950 cps sweep width. Removal of solvent from this filtrate yielded a white solid whose analysis was: H-3.39%, Be-3.70%, Al-25.6%, Cl-2.59%. A nujol mull of this solid had absorptions in the infrared at: 1816 (s,br.), 1606 (s,v.br.), 1350 (m,br.), 1170 (w), 1120 (w), 1017 (w), 969 (w), 846 (w), 740 (m,br.), 671 (w). The X-ray powder diffraction pattern of this solid consists of four lines also found in the product resulting by removing solvent from the reaction mixture $2LiAlH_4 + BeCl_2$ in tetrahydrofuran.

The insoluble residue of this reaction had the analysis: H-0.649%, Be-2.77%, Al-1.80%, Cl-44.2%. The infrared spectrum of a nujol mull of this solid had the following absorptions: 1805 (s,br.), 1683 (s,br.), 1544 (s,br.), 1322 (m,sh), 1238 (w), 1150 (m), 1058 (m, sh), 1029 (s), 986 (m), 967 (m), 855 (s,br.), 764 (s,br.), 723 (s,br.). The X-ray powder diffraction pattern contains the NaCl pattern plus a faint, indistinct line found in the pattern observed above for the soluble portion.

An attempt was made to detect the presence of butoxy-alane species in the soluble 2:1 product which had been equilibrated for 92 hours. Acid hydrolysis of the solid, followed by benzene extraction of the hydrolysate, confirmed the presence of 1-butanol when the extract was examined by vapor phase chromatography. The estimated aluminum/butanol ratio was slightly greater than one.

$LiAlH_4$ + $BeCl_2$ in 2:1 ratio in Tetrahydrofuran

To 32.1 mmoles of $BeCl_2 \cdot 2THF$ suspended in 200 ml of dry tetrahydrofuran was added 64.2 mmoles of $LiAlH_4$. No heat of reaction was noted, but most of the suspended halide dissolved immediately leaving a slightly turbid solution. Stirring at 25°C for 48 hours produced a completely clear, colorless, homogeneous solution. Removal of solvent until the volume was 100 ml caused no change. Approximately 100 ml of dry benzene was distilled into the solution, causing the appearance of a white precipitate. After removal of 50 ml of solvent by reduced pressure distillation, the solution was filtered to separate the white insoluble residue from the clear filtrate. The residue was shown to be pure LiCl (26 mmoles) by infrared and powder diffraction examination. Evaporation of the remainder of the solvent produced a gummy residue which solidified. The X-ray powder diffraction pattern of this solid showed the presence of additional LiCl plus nine other weak lines which could have arisen from a trace of $BeCl_2 \cdot 2THF$ or $LiAlH_4 \cdot nTHF$. The infrared spectrum of a nujol mull of this material showed the following absorption pattern: 1802 (s), 1023 (m), 842 (m), 752 (s), 725 (s), 623 (w), 528 (w).

Readdition of 100 ml of benzene to the product, followed by vigorous stirring, caused dissolution of some of the solid material. Filtration yielded a white residue and a colorless filtrate. The X-ray powder diffraction pattern of the white solid indicated the presence of LiCl plus lines found in the original sample before benzene addition. The infrared spectrum of this solid has the following absorptions: 1812 (s,br.), 1616 (s,v.br.), 1236 (m,br.), 1071 (m), 1028 (m), 859 (m), 843 (m), 753 (s), 605 (s), 534 (s). Removal of benzene solvent from the filtrate produces a gummy solid which would not solidify after prolonged pumping at 10^{-5} mm pressure, and for which no diffraction data could be obtained. The infrared spectrum of a nujol mull of this material was the same as that found for the original material before benzene addition, with the appearance of a broad band of low intensity at 1619 cm^{-1}.

Analysis of the benzene-insoluble portion of this reaction gave the following values: H-1.86%, Al-17.0%, Cl-37.4%. Analysis of the benzene-soluble product indicated the composition: H-1.68%, Be-4.47%, Al-16.6%, Cl-1.88%.

The 2:1 reaction between $LiAlH_4$ and $BeCl_2$ in tetrahydrofuran was repeated under conditions designed to minimize solvent cleavage. To 12.37 mmoles of $BeCl_2 \cdot 2THF$ was added 24.74 mmoles of $LiAlH_4$ in 225 ml of tetrahydrofuran. The reaction mixture temperature was maintained at 0°C with vigorous stirring for 15 hours, producing a slightly turbid solution. The turbidity vanished when the mixture was stirred at room temperature for two hours. Solvent was removed by reduced pressure distillation at low temperature. The solution remained clear until a

volume of 30 ml was reached, where a steadily increasing amount of solid began to precipitate. The final product was a white solid and was evacuated for 12 hours to remove excess solvent. The infrared spectrum of a nujol mull of this material had the following absorptions: 1808 (s,br.), 1616 (m,v.br.), 1017 (s), 852 (m), 730 (m), 621 (m). The X-ray powder pattern of this solid contains LiCl lines plus other well-defined lines which match the corresponding sample from the previous reaction, with the exception of four weak lines.

The reaction in the preceding paragraph was repeated and the residue isolated by solvent removal was extracted with benzene at room temperature for one hour. A white suspension resulted and filtration produced a white residue and a clear filtrate. The infrared spectrum of the insoluble residue exhibited the following absorptions: 1765 (s, br.), 1350 (m,br.), 1007 (w), 841 (w,br.), 1718 (w), 669 (s), 400-200 (s,br.). Evaporation of benzene from the filtrate produced a white solid with the following analysis: H-3.19%; Al-28.5%; Cl-5.22%, beryllium concentration was too small to measure accurately; no lithium was found by flame photometric analysis. The infrared spectrum of this product had the following absorptions: broad strong absorption from 2000 to 1300 cm^{-1}; 1169 (w), 1079 (m), 910 (w), 716 (w), 669 (w), 246 (m).

$LiAlH_4$ + $BeCl_2$ in 1:1 Ratio in Tetrahydrofuran

$LiAlH_4$ (28.9 mmoles) was added dropwise to a stirred suspension of 28.9 mmoles of $BeCl_2$ in 200 ml of tetrahydrofuran at 25°C. The suspended crystals of $BeCl_2 \cdot 2THF$ dissolved immediately, leaving a

slightly turbid solution. Stirring for 15 hours yielded a perfectly clear, homogeneous solution. Distillation of 150 ml of benzene into the reaction mixture left it unchanged. Removal of solvent at reduced pressure until the total volume is approximately 20 ml caused the appearance of a precipitate which was identified as LiCl upon isolation. The filtrate precipitated more LiCl on standing. Removal of the remainder of the solvent yielded a gummy solid which solidified after prolonged pumping at 0.5 mm pressure. The infrared spectrum of this solid had absorptions at: 1877 (m), 1802 (s), 1781 (s), 1618 (m,v.br.), 1238 (w), 1170 (w), 1115 (w), 1060 (m), 1028 (s), 967 (s), 916 (w), 875 (w), 754 (m), 657 (m), 580 (w), 460 (m). The X-ray powder pattern indicated the presence of LiCl plus many additional lines which did not match $BeCl_2 \cdot 2THF$.

The addition of 60 ml of dry benzene to this solid produced a white slurry which was stirred for several hours and filtered. The white residue obtained had the following infrared spectrum: 1880 (w, br.), 1830 (w,br.), 1539 (s,br.), 1189 (m,br.), 1122 (w), 1062 (m), 998 (w), 972 (w), 898 (m), 803 (w), 724 (s), 563 (s), 338 (w). The X-ray powder diffraction pattern indicated the presence of LiCl plus seven unidentified lines. Analysis of the solid indicated the composition: H-1.26%, Be-0.764%, Al-13.4%, Cl-35.42%. Removal of benzene from the filtrate yielded a gummy solid which would not solidify with prolonged pumping at reduced pressure with heating (65°C, 24 hours). Slight discoloration of the material was noted along with some gas evolution, and the product was finally characterized as a plastic mass. Analysis of this product gave the following values: H-0.716%, Be-4.70%,

Al-10.2%, Cl-16.1%. The infrared spectrum of a nujol mull of this product before heating at reduced pressure was: 1876 (s), 1810 (s), 1780 (sh), 1312 (w), 1267 (w), 1240 (w), 1169 (m), 1153 (w), 1116 (m), 1060 (s), 1028 (s), 965 (w), 948 (w), 901 (w), 843 (w), 760 (w,br.), 722 (w,br.), 664 (w), 570 (w,sh), 463 (s). The infrared spectrum of a nujol mull of the same sample after heating and evacuation shows the following absorptions: 1876 (s,br.), 1803 (s,sh), 1348 (w), 1306 (w), 1258 (m), 1238 (m), 1166 (s), 1114 (m), 1056 (s), 1023 (s,br.), 959 (s,br), 898 (m), 826 (s,br), 642 (s,br), 573 (m,sh), 525 (m), 458 (s).

The reaction was repeated in tetrahydrofuran at 0°C using 8.46 mmoles of $BeCl_2$ and 8.46 mmoles of $LiAlH_4$ in 150 ml of tetrahydrofuran. The mixture was stirred for 15 hours at 0°C yielding a slightly turbid solution. Removal of solvent at reduced pressure caused no solid precipitation until approximately 50% of the solvent had been removed. The final product of solvent removal was a gummy solid. Thirty-nine hours of pumping at reduced pressure (0.1 mm, 25°C) yielded a plastic solid whose infrared spectrum was: 1778 (vs,br), 1575 (sh), 1237 (m), 1170 (s), 1110 (w), 1005 (s), 960 (m), 920 (s), 840 (s,br.). Continued pumping (24 hours) finally yielded a white powder whose infrared spectrum as a nujol mull was the following: 1802 (s,br.), 1619 (s,br.), 457 (w), plus an irregular baseline which showed no definite absorptions. The powder diffraction pattern of this solid indicated the presence of LiCl plus 11 additional lines which do not match $BeCl_2 \cdot 2THF$.

$NaAlH_4$ + $BeCl_2$ in 1:1 Ratio in Tetrahydrofuran

To a stirred suspension of 15.6 mmoles of $BeCl_2 \cdot 2THF$ in 150 ml

of tetrahydrofuran was added 15.6 mmoles of $NaAlH_4$. The reaction was cooled in an ice-water bath as the addition was made, and the mixture was stirred for 30 minutes prior to filtration. A white precipitate formed as the reagents were combined. Filtration produced a white solid residue and a clear filtrate. Removal of solvent from the filtrate by reduced pressure distillation, in the cold, gave a white solid.

Analysis of the insoluble product gave the following: H-0.806%, Be-2.94%, Al-1.28%, Cl-43.4%. The infrared spectrum of a nujol mull of the solid had absorptions at the following positions: 1729 (s,br.), 1350 (m,v.br.), 1011 (s), 955 (w), 912 (w), 863 (s), 730 (m,br.), 542 (m,br.). The X-ray powder diffraction pattern shows the presence of $BeCl_2 \cdot 2THF$ and NaCl with three unidentified weak lines. Analysis of the solid isolated from the soluble portion of the reaction mixture indicated the following composition: H-2.72%, Be-4.08%, Al-21.2%, Cl-15.8%. The infrared spectrum of a nujol mull of this solid had the following absorptions: 1874 (s,br.), 1573 (s,v.br.), 1160 (m,br.), 1019 (s,br.), 950 (s,br.), 829 (s,br.), 712 (s,br.), 649 (s,br.), 452 (m,br.), 369 (w), 343 (w). The X-ray powder diffraction pattern of this solid does not confirm the presence of $BeCl_2 \cdot 2THF$ or NaCl, but has many lines.

$LiAlH_4$ + $BeCl_2$ in 1:1 Ratio in Diethyl Ether

$LiAlH_4$ (25.03 mmoles) was added dropwise to 25.03 mmoles of $BeCl_2$ in 250 ml of diethyl ether at 0°C. A precipitate formed immediately. Stirring for 18 hours produced a clear supernatant solution over a flocculent precipitate. Filtration yielded a white solid and a

clear filtrate. Removal of solvent from the filtrate produced a clear glass puddle which disintegrated upon further evacuation to a powder having a crystalline appearance.

Analysis of the insoluble material from this reaction gave the following results: H-2.46%, Be-8.37%, Al-3.25%, Cl-62.2%. The powder diffraction pattern of the solid indicated the pattern of LiCl plus three additional weak lines. The infrared spectrum of a nujol mull of this solid had the following absorptions: 1758 (s,v.br.), 1350 (m,v. br.), 1022 (w), 778 (m,v.br.). Analysis of the soluble product indicated the composition: H-2.65%, Be-3.58%, Al-23.0%, Cl-26.1%. The infrared spectrum of a nujol mull of this product exhibits absorptions at: strong, broad band from 2200 to 1200 cm^{-1}, 1190 (w), 1150 (w), 1091(w), 1023 (w), 973 (w), 890 (w), 844 (w), 760 (w), 600 (w,br.), 444 (w). The X-ray powder pattern consisted of four diffuse lines which match those found for the 2:1 case, soluble species.

The reaction was repeated at -78°C using 22.7 mmoles of $BeCl_2 \cdot 2Et_2O$ and 22.7 mmoles of $LiAlH_4$ in 200 ml of diethyl ether. Again a precipitate formed immediately. After stirring for 45 minutes, filtration in the cold produced a white solid and a clear filtrate. Removal of the solvent from the filtrate produced a white solid.

Analysis of the insoluble residue gave the following composition: H-2.08%, Be-9.03%, Al-3.46%, Cl-58.1%. The infrared spectrum of a nujol mull of the insoluble solid had the following absorptions: 1765 (s,v. br.), 1350 (m,v.br.), 1190 (w), 1150 (w), 1085 (w), 1017 (m), 890 (w), 841 (w), 773 (m). The X-ray powder pattern showed the LiCl pattern

plus one weak, unidentified line. The solid isolated from the soluble portion of this reaction mixture gave the analysis: H-3.25%, Be-1.08%, Al-28.2%, Cl-24.0%. The infrared spectrum of a nujol mull of this solid exhibited absorptions at: 1851 (m,v.br.), 1615 (m,v.br.), 1257 (w), 1187 (w), 1145 (w), 1086 (w), 1014 (w), 968 (w), 888 (w), 730 (m,br.), 620 (w), 443 (w). The X-ray powder diffraction pattern contains four weak lines.

Solution Spectra: $LiAlH_4$ + $BeCl_2$ in Diethyl Ether

Molar increments of $LiAlH_4$ were added to 9.23 mmoles of $BeCl_2$ dissolved in 50 ml of diethyl ether. After the hydride addition, the mixture was stirred for 30 minutes to 1 hour, the precipitate allowed to settle, and samples (1 ml) of the clear supernatant were withdrawn by syringe for infrared examination. Absorptions at 1:1 = hydride: halide ratio were: (solvent bands omitted) 1848 (s), 1787 (s), 1638 (w), 964 (m), 904 (m), 764 (s), 712 (s), 569 (w), 502 (w). These bands were unchanged on stirring for 16 hours. Absorptions at 2:1 ratio were 1811 (s,sh.), 1787 (s), 1638 (w), 900 (w), 753 (s), 675 (m), 540 (w). Absorptions at 3:1 ratio were: 1812 (s,sh.), 1785 (s), 1747 (s), 900 (w), 754 (s), 685 (m), 540 (w). Filtration of the mixture produced a white residue which had the following spectrum after drying at reduced pressure: 1754 (s,br.), 1350 (m,br.), 1025 (w), 752 (s,br.). The powder diffraction pattern of this solid showed only LiCl and a single additional, indistinct line. Removal of ether from the clear, colorless filtrate produced a white solid having the infrared spectrum: 1778 (s,br.), 1618 (s,br.), 1147 (w), 1026 (s), 891 (m,sh.), 802 (w, sh.), 720 (s,br.), 600 (s). The X-ray powder diffraction pattern of

this solid contained eight lines. A sample of $LiAlH_4$ solution was stripped of solvent at 25°C to yield a white solid whose infrared spectrum was: 1778 (s,br.), 1666 (s,br.), 1148 (w), 867 (s,br.), 714 (s,br.). The X-ray powder pattern of this partially desolvated hydride did not match the pattern for the ether-soluble product described above. The soluble reaction product was unstable and decomposed to a dark gray solid with gas evolution.

Solution Spectra: $LiAlH_4$ + $BeCl_2$ in Tetrahydrofuran

$LiAlH_4$ solution was added to 4.54 mmoles of $BeCl_2$ in 50 ml of tetrahydrofuran. Spectra were recorded from samples of the clear, homogeneous solution. Absorptions at 0:1 ratio: 665 (s,sh.), 574 (m), 524 (w). Absorptions at 1:1 ratio: 1730 (s,br.), 773 (m), 729 (m), 670 (s,sh.), 378 (w). Absorptions at 2:1 ratio: 1730 (s,sh.), 1701 (s), 776 (s), 731 (w), 680 (m,sh.), 370 (m,br.). Absorptions at 3:1 ratio: 1730 (s,sh.), 1695 (s), 1646 (m,sh.), 774 (s), 731 (w), 680 (m,sh.), 370 (m,br.). Absorptions at 7:1 ratio: 1691 (s), 1646 (s, sh.), 763 (s), 733 (m,sh.), 679 (m), 530 (w), 384 (s). Absorptions of $LiAlH_4$ solution: 1691 (s), 763 (s), 390 (m).

Solution Spectra: $NaAlH_4$ + $BeCl_2$ in Tetrahydrofuran

The procedure was the same as above except that the precipitate formed would not settle on standing for one hour. At 2:1 ratio, the mixture was filtered and the infrared spectrum of the filtrate examined. Absorptions were found at: 1736 (s), 1269 (w,sh.), 797 (w), 724 (m). $NaAlH_4$ in tetrahydrofuran has absorptions at 1680 and 772 cm^{-1}.

Instrumentation

Infrared spectra were obtained on a Perkin-Elmer, Model 621, grating infrared spectrophotometer. Samples were prepared as nujol mulls or as ethereal solutions and were scanned from 2300 to 200 cm^{-1} using CsI cell windows.

Nmr spectra were recorded on a Varian Associates A60 nuclear magnetic resonance spectrometer (60 mc).

X-ray powder diffraction data were obtained using a Debye-Scherrer camera (Norelco, 114.6 mm) and Cu(Kα) radiation (1.5418 Å) with a nickel beta filter. Also, Mo(Kα) radiation (0.7107 Å) with a zirconium beta filter was employed. The samples were loaded into thin-walled Lindemann glass capillaries (0.5mm) in the dry box.

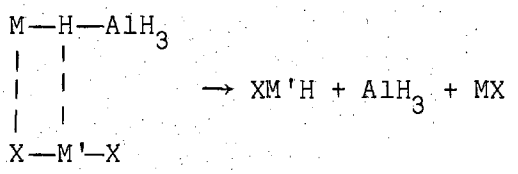
CHAPTER III

RESULTS AND DISCUSSION

The reaction between complex aluminum hydrides $MAlH_4$ (where M = Li,Na,K,Cs) and metal halides of Group II, $M'X_2$ (where M' = Be, Mg,Ca,Zn,Cd,Hg; X = Cl,Br,I), may be described in two ways. The first of these descriptions would be the simple metathetical exchange shown in Equation 5. The complex aluminum hydride in this case is presumed to exist

$$2\ MAlH_4 + M'X_2 \rightarrow 2\ MX + M'(AlH_4)_2 \qquad (5)$$

as a solvent-separated ion pair. The second description employs a subtle difference in the constitution of the hydride reactant, i.e., the complex aluminum hydride may be thought of as an MH species coordinated to AlH_3 through a hydrogen bridge. Reaction of this bridged hydride species with $M'X_2$ might then occur by a different mechanism as shown in Equation 6, to form $M'H_2$ directly instead of $M'(AlH_4)_2$. Experimental verification of either of these two postulated processes is complicated by the possibility of a redistribution-



$$XM'H + MAlH_4 \rightarrow M'H_2 + AlH_3 + MX \quad (6)$$

disproportionation equilibrium (equation 7) which may be attained rapidly or very slowly.

$$M'(AlH_4)_2 \rightleftarrows M'H_2 + 2\ AlH_3 \quad (7)$$

The only alkali metal aluminum hydride which is soluble in diethyl ether is $LiAlH_4$. This unique behavior is attributed to strong solvation of the small lithium cation by the moderately basic ether. Where the cation is larger (Na or K) a more basic solvent, such as tetrahydrofuran, is required for solubilization. In the case of $CsAlH_4$, only a difunctional ether, such as diglyme, acts as a solvent. In general, it may be argued that solubility of these compounds is dependent upon effective solvation of the cation and that for small cations a less basic solvent is required than for large cations. On the other hand, $[(n\text{-}C_8H_{17})_3(n\text{-}C_3H_7)N]AlH_4$ is soluble in benzene (10) whereas $[(CH_3)_4N]AlH_4$ is not soluble in any organic solvents. The

solubility of the former is probably due to the long alkyl chains on the ammonium cation; when such groups are absent, solubility is lost in hydrocarbon solvents due to poor solvation of the $(CH_3)_4N^+$ cation by benzene.

The infrared spectra of complex aluminum hydrides and other alane derivatives are complicated in some instances, but some useful, general statements can be made. Terminal Al-H stretching frequencies occur between 1912 cm^{-1} and 1660 cm^{-1}, and may be lower in bridging situations (1550 cm^{-1}). Deformation modes of AlH_4^- are observed at ca. 750 cm^{-1}. Shifts in Al-H stretching frequencies have been correlated with the increase or decrease of the coordination number of aluminum. In general, increasing coordination number for aluminum will cause the Al-H stretching frequency to decrease (11); those compounds of coordination number five absorb below 1750 cm^{-1} and those of coordination number four absorb above 1750 cm^{-1}. Dilts (12) has discussed the shift in the Al-H stretching frequency in terms of covalent interactions for selected derivatives of complex aluminum hydrides.

Reactions in Diethyl Ether

Because of solubility, $LiAlH_4$ was the only hydride reacted with $BeCl_2$ in diethyl ether. Analytical data are summarized in Tables 1 and 2 for reactions at 25°C and -78°C.

The reactions of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio are rapid and complete within one hour at -78°C. Aluminum hydride is recovered virtually uncontaminated, except by residual solvent, from the soluble fractions of the reaction mixture. The infrared spectrum of the

Table 1. $LiAlH_4$ + $BeCl_2$ in Diethyl Ether at 25°C

$LiAlH_4$:$BeCl_2$	Solubility of Product	H:Al	(Total H^- Less AlH_3):Be	Be:Cl
1:1	soluble	3.08:1.0	1.0:5.22	1.0:1.85
1:1	insoluble	20.2:1.0	2.24:1.0	1.0:1.89
2:1	soluble	3.12:1.0	no Be	no Be
2:1	insoluble	11.0:1.0	2.22:1.0	1.0:2.0

Table 2. $LiAlH_4$ + $BeCl_2$ in Diethyl Ether at -78°C

$LiAlH_4$:$BeCl_2$	Solubility of Product	H:Al	(Total H^- Less AlH_3):Be	Be:Cl
1:1	soluble	3.09:1.0	1.0:2.22	1.0:2.84
1:1	insoluble	16.2:1.0	1.69:1.0	1.0:1.64
2:1	soluble	3.18:1.0	no Be	no Be
2:1	insoluble	10.5:1.0	2.06:1.0	1.0:2.05

reaction solution has a strong absorption at 1787 cm^{-1}, which does not agree closely with the value of 1801 cm^{-1} observed by Erlich (13) for a metastable alane solution prepared from $LiAlH_4$ and $AlCl_3$ using the method of Finholt, et al. (14). Aluminum hydride prepared in diethyl ether by this latter reaction precipitates from solution within minutes after its separation from the LiCl by-product. In contrast, the AlH_3 generated by $LiAlH_4$-$BeCl_2$ interaction is stable in solution over a period of at least 135 hours at room temperature. It appears that AlH_3 is being solubilized by the presence of solid LiCl or BeH_2 according to an equilibrium of the type shown in equation (8). The infrared spectrum of the solid AlH_3 etherate which was isolated from the 2:1

$$\underset{\text{solid}}{L} + AlH_3 \rightleftarrows [L\cdot AlH_3] \rightarrow AlH_3 + \underset{\text{solution}}{L\downarrow} \qquad (8)$$

(where L = LiCl, BeH_2)

reaction had broad absorptions at 1755, 1660 cm^{-1} (25°) and 1778, 1600 cm^{-1} (-78°). The reported spectra (11) for $AlH_3\cdot xEt_2O$ show absorptions at 1760 and 1592 cm^{-1} as nujol mulls. The varying values of the absorption maxima arise from the extreme broadness of the bands and undoubtedly from slightly differing residual solvent content.

The insoluble products of the 2:1 reaction are LiCl and $BeH_2\cdot xEt_2O$. The infrared spectrum of the insoluble solid exhibits a strong, broad band at 1755 cm^{-1} (25°C) and 1750 cm^{-1} (-78°C). The infrared spectrum of BeH_2 prepared by pyrolysis of $Be(BH_4)_2$ with $(C_6H_5)_3P$ in 2:1 ratio has a strong, broad Be-H stretching absorption at 1758 cm^{-1};

the product gave no X-ray powder diffraction pattern (15). For the product isolated as the insoluble solid in the 2:1 reaction, only lines arising from LiCl were noted in the X-ray powder diffraction pattern. Analytical data indicate a Be:H ratio of 1:2.

Thus, the original report by Wiberg (1) appears to be incorrect, and the work of Holley and Lemons (3) corroborated. The findings of Wood and Brenner (2) could not be substantiated since no $Be(AlH_4)_2$ was generated which could be stabilized at low temperatures. Also, we found no evidence for $LiBe(AlH_4)_3$ species (4) in reactions between $LiAlH_4$ and $BeCl_2$ in diethyl ether.

The Russian claim (23) concerning the preparation of $LiAl_2H_7$ could not be verified. Analysis of this new compound gave the elemental ratios: Li:Al:H = 1.0:2.19:7.0; the powder diffraction pattern was also reported. It is notable that the Al:H ratio of this product is only 1.0:3.2, and seems to be inconsistent with the reported empirical formula. We have found less than 0.8 per cent lithium in the soluble products of the 2:1 reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether and an Al/Li ratio of approximately 17. X-ray powder diffraction data for these soluble products do not match those from the Russian report. The powder pattern of AlH_3 etherate which we have isolated from this 2:1 reaction at 25°C does agree well with the powder pattern of an alane etherate reported by French workers (24) to be a limiting composition of desolvation efforts with $AlH_3 \cdot nEt_2O$.

For the reactions where the $LiAlH_4$:$BeCl_2$ ratio is 1:1, the reaction is more complex. The infrared data, elemental analysis, and X-ray powder diffraction pattern of the insoluble reaction product show

that the major constituents are LiCl and BeH_2. Analysis of the soluble portion of the reaction indicates a mixture of AlH_3 and $BeCl_2$, but it is probable that such a mixture would react further according to equations (9) and (10).

$$AlH_3 + BeCl_2 \rightarrow H_2AlCl + HBeCl \quad (9)$$

$$HBeCl + H_2AlCl \rightarrow HAlCl_2 + BeH_2\downarrow \quad (10)$$

Such interactions would preserve the amount of soluble chloride and hydride if the hydridoberyllium compounds were either soluble or were complexed by the halogen-alane species which are soluble. Some support for AlH_3-$BeCl_2$ interactions is found in the infrared spectrum of the reaction solution itself, where a band at 1848 cm^{-1} is observed at 1:1 ratio only. The spectrum does not change after 16 hours of stirring. The triethylaminate of H_2AlCl is known to absorb at 1852 cm^{-1} in benzene, whereas the aminate of $HAlCl_2$ absorbs at 1898 cm^{-1} (17). Thus, the most likely interaction would produce H_2AlCl and HBeCl, the latter being an unreported compound.

Infrared data on solutions of $LiAlH_4$ and $BeCl_2$ where the ratio of these reactants is greater than 2:1 indicates only an increase in the absorption due to $LiAlH_4$.

Reactions in Tetrahydrofuran

Both $NaAlH_4$ and $LiAlH_4$ were allowed to react with $BeCl_2$ in tetrahydrofuran. Of the alkali halide by-products, NaCl is insoluble while LiCl is soluble.

The reaction of $LiAlH_4$ with $BeCl_2$ in both 1:1 and 2:1 ratios yields a mixture of products which are soluble. Fractional crystallization of the product solution deposited only pure LiCl and no evidence of BeH_2 deposition was observed. The infrared spectra of the product solutions exhibit an Al-H stretching band at 1730 cm^{-1} for a 1:1 ratio of reactants, 1701 cm^{-1} with a shoulder at 1730 cm^{-1} for 2:1 ratio, 1695 cm^{-1} with a shoulder at 1730 cm^{-1} for 3:1 ratio, and 1691 cm^{-1} at 7:1 ratio. $LiAlH_4$ in tetrahydrofuran absorbs at 1691 cm^{-1}. Aluminum hydride in tetrahydrofuran solution is reported to absorb at 1739 cm^{-1} (18) and 1724 cm^{-1} (13). The infrared spectrum of the product mixture after solvent removal exhibited Al-H stretching vibrations at 1808, 1616 cm^{-1} (2:1 mixture), and 1802, 1619 cm^{-1} (1:1 mixture). These are very close to the values expected for the tetrahydrofuranate of AlH_3 which absorbs at 1802 cm^{-1} (11) or 1810 cm^{-1} (18). Thus, on the basis of the infrared data it is difficult to distinguish the reaction products from $AlH_3 \cdot xTHF$ since the bands are so broad. On the other hand, the fact that BeH_2 does not precipitate demonstrates clearly that a strong interaction is present. Since pure LiCl may be precipitated by the addition of a non-coordinating solvent such as benzene, the interaction products are suggested to be $Be(AlH_4)_2$ (2:1 reaction) or $ClBeAlH_4$ (1:1 reaction).

Using $NaAlH_4$ in tetrahydrofuran gives different results. The analytical data for reactions between $NaAlH_4$ and $BeCl_2$ in tetrahydrofuran are summarized in Tables 3 and 4.

At a $NaAlH_4$:$BeCl_2$ ratio of 2:1, the initial products are analogous to those found for the $LiAlH_4$:$BeCl_2$ = 2:1 reactions in diethyl

Table 3. $NaAlH_4$ + $BeCl_2$ in Tetrahydrofuran (0°C)

$NaAlH_4$:$BeCl_2$	Solubility of Product	H:Al	(Total H^- Less AlH_3):Be	Be:Cl
1:1	soluble	3.47:1.0	1.0:1.23	1.02:1.0
1:1	insoluble	16.9:1.0	1.0:1.23	1.0:1.52
2:1	soluble	3.14:1.0	1.0:1.23	8.40:1.0
2:1	insoluble	19.2:1.0	1.84:1.0	1.0:2.13

Table 4. $2NaAlH_4$ + $BeCl_2$ in Tetrahydrofuran (25°C, 92 Hours)

$NaAlH_4$:$BeCl_2$	Solubility of Product	H:Al	(Total H^- Less AlH_3):Be	Be:Cl
2:1	soluble	3.57:1.0	1.32:1.0	5.62:1.0
2:1	insoluble	9.73:1.0	1.46:1.0	1.0:4.05

ether. The soluble reaction product is predominantly $AlH_3 \cdot xTHF$ and is identified by its analysis and by the infrared spectrum which has strong hydridic absorptions at 1800 cm^{-1} and 1625 cm^{-1}. The insoluble reaction products are NaCl and BeH_2, the hydride Be-H stretching frequency being reduced to 1710 when the product is isolated from tetrahydrofuran. Stirring the 2:1 reaction mixture for 92 hours caused solubilization of the BeH_2 from the insoluble phase to the soluble portion of the reaction mixture. It is postulated that this interaction is of the type shown in equation (11). The infrared spectrum of the equilibrated solution

$$2AlH_3 + BeH_2 \rightarrow Be(AlH_4)_2 \qquad (11)$$

had a strong absorption at 1740 cm^{-1}, very close to the initial value of 1736 cm^{-1} which appears immediately after mixing. The solid obtained by removing solvent from this equilibrated solution exhibited Al-H stretching bands at 1816 cm^{-1} and 1606 cm^{-1}. This product is very similar to the soluble product from the 2:1 $LiAlH_4$ reaction, on the basis of infrared spectra and X-ray powder diffraction patterns.

The observation that the 2:1 reaction in tetrahydrofuran proceeds in a different manner for $LiAlH_4$ than for $NaAlH_4$ has two implications. The first consideration is the possibility that the compositions of these two hydrides are different in tetrahydrofuran solution and that each hydride species leads to a separate product mixture. The second possibility is that the LiCl by-product is able to solubilize BeH_2 readily whereas NaCl is ineffective in such a process.

The comparative degree of cation solvation should be the discriminating effect for these two hydrides in solution. The Al-H stretching vibrations for $LiAlH_4$ and $NaAlH_4$ in tetrahydrofuran solution are 1691 cm^{-1} and 1680 cm^{-1}, respectively. This is not a large change but indicates less cation-anion, covalent interaction when sodium is the cation. At the present time, little else is known about the composition of these hydrides in solution and it must be concluded that there is no evidence for significant differences in these two reagents in tetrahydrofuran which would justify proposal of more than one reaction mechanism with $BeCl_2$.

On the other hand, LiCl is known to form soluble complexes with halogen-alane species in diethyl ether (17) and evidence for LiBr-AlH_3 and LiI-AlH_3 adducts has been found in diethyl ether and tetrahydrofuran (20,21). Therefore, it is quite reasonable that LiCl would form a complex with BeH_2 and prevent its precipitation in the $LiAlH_4$-$BeCl_2$ reaction in tetrahydrofuran. This adduct could then react further with AlH_3 to produce $Be(AlH_4)_2$ as shown in equation (12).

$$LiBeH_2Cl + 2AlH_3 \rightarrow LiCl + Be(AlH_4)_2 \qquad (12)$$

$$(\text{or } Li_2BeH_2Cl_2)$$

When solvent is removed from a 2:1 mixture of $LiAlH_4$ and $BeCl_2$ in tetrahydrofuran, a white residue results. If this residue is extracted with benzene, the soluble product is solvated AlH_3 and not $Be(AlH_4)$. This result lends further support to the hypothesis that

BeH_2 and AlH_3 are present in the solution, BeH_2 being solubilized by a process such as that described above.

The 2:1 reaction between $NaAlH_4$ and $BeCl_2$ in tetrahydrofuran produces soluble AlH_3 and an insoluble mixture of BeH_2 and NaCl. Attempted benzene extraction of solvated $Be(AlH)_4$ from the reaction product of $LiAlH_4$ and $BeCl_2$ in tetrahydrofuran in 2:1 ratio yielded only solvated alane in 56 per cent yield as the soluble product. Therefore, no evidence of $Be(AlH_4)_2$ was found as the initial product of these reactions. In ether solvents, if $Be(AlH_4)_2$ is formed initially, disproportionation appears to be the predominant fate of this species. The observed redistribution of the products from the 2:1-$NaAlH_4$:$BeCl_2$ reaction in tetrahydrofuran could be explained as being due to catalysis by alkoxy-alane species arising from attack of AlH_3 on the solvent.

Again, the 1:1 reactions with $NaAlH_4$ in tetrahydrofuran are more complex than the 2:1 reactions. The insoluble product mixture was found to contain NaCl, BeH_2, and $BeCl_2 \cdot 2THF$ as the principal components. The soluble product does not contain $BeCl_2 \cdot 2THF$, and has an infrared absorption maximum at 1874 cm^{-1} and 1573 cm^{-1}. Analytical data suggests that the soluble species are AlH_3 and a compound of empirical formula HBeCl, possibly in combination as $ClBeAlH_4$; however, the Al:Be ratio is 1.73:1.0. Extended equilibration time might permit the insoluble product to react further to yield as final products, soluble $ClBeAlH_4$ and insoluble NaCl. The shift of the Al-H stretching frequency for this soluble 1:1 product to a value ca. 55 cm^{-1} above that for the

absorption of the corresponding 2:1 product may reflect the effect of substituting chloride for aluminohydride in the proposed $Be(AlH_4)$. A corresponding shift is not observed for $Mg(AlH_4)_2$ and $ClMgAlH_4$ from tetrahydrofuran (5).

CHAPTER IV

CONCLUSIONS

Lithium aluminum hydride and $BeCl_2$ in 2:1 ratio were found to react in diethyl ether according to equation (13). In 1:1 ratio in

$$2LiAlH_4 + BeCl_2 \rightarrow BeH_2\downarrow + 2LiCl\downarrow + 2AlH_3 \qquad (13)$$

diethyl ether, evidence was presented for the reaction scheme shown in equations (14) and (15).

$$LiAlH_4 + BeCl_2 \rightarrow \tfrac{1}{2}BeH_2\downarrow + LiCl\downarrow + AlH_3 + \tfrac{1}{2}BeCl_2 \qquad (14)$$

$$BeCl_2 + AlH_3 \rightarrow HBeCl + ClAlH_2 \qquad (15)$$

In tetrahydrofuran, both $LiAlH_4$ and $NaAlH_4$, in 2:1 ratio with $BeCl_2$, appear to react according to equations (16) and (17). No evidence for $Be(AlH_4)_2$ as an initial product was found. The insoluble BeH_2 product of equation (16) was partially dissolved on prolonged

$$2NaAlH_4 + BeCl_2 \rightarrow 2AlH_3 + BeH_2\downarrow + 2NaCl\downarrow \qquad (16)$$

$$2LiAlH_4 + BeCl_2 \rightarrow 2AlH_3 + [2LiCl\cdot BeH_2] \qquad (17)$$

stirring of the solution; however, the soluble product was contaminated by tetrahydrofuran cleavage products. The data for reactions of $LiAlH_4$ or $NaAlH_4$ with $BeCl_2$ in 1:1 ratio in tetrahydrofuran support the descriptions shown in equations (18) and (19).

$$LiAlH_4 + BeCl_2 \rightarrow AlH_3 + HBeCl + LiCl \qquad (18)$$

$$NaAlH_4 + BeCl_2 \rightarrow AlH_3 + HBeCl + NaCl\downarrow \qquad (19)$$

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